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THE

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# REPORTS

OF THE

# ROYAL COLLEGE OF CHEMISTRY,

AND

# RESEARCHES

CONDUCTED IN THE LABORATORIES

IN THE YEARS 1845–6–7.

LONDON

MDCCCXLIX.

LONDON:
Printed by Schulze and Co., 13, Poland Street.

27 MY 10 A.P.S.
Rec'd 3-19-34 W.C.

# PREFATORY REMARKS.

The Council of the Royal College of Chemistry have long felt an anxious desire to respond to the expressed wish of the Members, to possess some further account of the proceedings of the Institution than that contained in the Annual Reports. There were, however, difficulties, at an earlier period, opposed to a compliance with this natural desire on the part of the Members and friends of the College, of which they could not be aware; the somewhat uncertain position of the Institution, the form it should assume, and the purely scientific character of the researches, were opposed to the publication of such a Report as would satisfy the Members, and, at the same time, promote the interests of the College. The Council are now happy to state, that the obstacles they had to contend with have nearly vanished, that the present position of the College is highly satisfactory, and its future prospects most encouraging.

Reclass 3-30-34 NKP.

Although the Annual Reports of the Council were circulated among the Members, it has been thought right to republish here some Extracts from those Reports, in order to recal to their minds the objects the Founders had in view in establishing a Practical School of Chemistry in England,—to point out the advantages the country must derive from an institution devoted

to the cultivation of Scientific Chemistry, under the direction of a Professor of established reputation, and also to make the Subscribers aware of some of the difficulties the Council have had to contend with in bringing the College to its present gratifying position.

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## EXTRACTS FROM THE FIRST REPORT OF THE COUNCIL. NOVEMBER, 1846.

"The College was first established by a public meeting held in St. Martin's Place, on the 29th of July, 1845. A form was then given to the new Institution, by the election of a Council, with power to add to their number, and by the appointment of certain executive officers under the control of the Council. Great labour and many difficulties were inseparable from carrying out a design, then only in its infancy, and deficient in almost every thing that was necessary for the permanent working of such an Institution.

"The first and paramount object, necessary to the success of the undertaking, was the appointment of a Professor. This had been the subject of anxious consideration with the Provisional Council, previous to the public meeting, and the new Council lost no time in taking steps to conclude an agreement with Dr. Hofmann, of the University of Bonn, whose growing reputation had already attracted the notice of scientific chemists throughout Europe. Some obstacles presented themselves to Dr. Hofmann's accepting the appointment; but by the influence of His Royal Highness Prince Albert, who had condescended himself to be named President of the College, these were overcome. And here the Council cannot help

remarking, that no circumstance, connected with the whole proceedings of the Institution, has given such unmixed satisfaction to those who have anxiously watched its progress, as the appointment of their able Professor.

"The next object of the Council was to make arrangements for opening the school. Rooms were hired and fitted up as Laboratories, in George Street, Hanover Square, which enabled the Professor to commence the operations of the Practical School in October, 1845. Some inconvenience resulted from the imperfect nature of these Laboratories, but the grand object of demonstrating that the Council were in earnest in establishing, on a broad and scientific basis, a Practical School of Chemistry in London, has been fully accomplished; and the fact that upwards of twenty students enrolled themselves within a week of its being opened, afforded sufficient evidence of the want of such a school.

"The opening of the school in these temporary Laboratories having been effected, the Council proceeded to look forward to a more convenient and permanent habitation for the College.

"Encouraged by the promises of support they had received, and backed by the guarantee of several noblemen and gentlemen, the Council took premises in Hanover Square. This site not only possessed the advantages of a good and ostensible position, affording all necessary accommodation for the official purposes of the College, the residence of the Professor and Secretary, and the meetings of members, but supplied the desideratum of a large piece of ground, with a frontage to Oxford Street, whereon convenient and well-arranged Laboratories could be erected. An agreement for a lease was drawn up, and the necessary covenants arranged, Mr. Malcolm, the owner of the property, having been previously made acquainted

with the purposes to which the premises were to be applied. At this stage of their progress, the Council had the gratification of receiving a communication from Sir James Graham, then Secretary of State for the Home Department, to the effect that Her Majesty had been pleased to express her commands, that the College should be designated THE ROYAL COLLEGE OF CHEMISTRY.

"Alive to the imperfections of the temporary School in George Street, the construction of the new Laboratories was an object of anxious consideration with the Council, and the most eminent Architects and Chemists were consulted as to the formation of an economical and convenient edifice, and the most efficient arrangements for the operations of the Laboratory. At length the Council were satisfied that these ends would be attained in the plan which they had adopted; and the first stone of the New Building was laid on the 16th of June, 1846, by His Royal Highness Prince Albert, in the presence of a large and distinguished meeting of the members and friends of the College, His Royal Highness expressing his most cordial concurrence in the design. From that time, the works proceeded rapidly, under the able superintendence of their Architect, Mr. Lockyer, and the buildings are now completed to the entire satisfaction of those appointed to superintend the works.

"As will naturally be expected, in the endeavour to institute such an establishment as the Royal College of Chemistry, which promises to take its place amongst our most important National Institutions, serious outlay has been unavoidable. Still the Council have the satisfaction to report, that the School is at this moment in a most flourishing condition, and they do not hesitate to express their confidence in the continued success of the establishment. That the Council have fair grounds for

this confidence, is evinced in the gratifying fact, that their Royal President continues to take a lively interest in the progress of the College, of which His Royal Highness has given a substantial proof, in a donation of £100 to the Building Fund, in addition to the like sum to the fund for general purposes; and that among the Vice-Presidents and Members of Council are to be found some of the most distinguished and influential men of the country. They cannot help also referring to the list of liberal donors to the Building Fund, as a proof of the warm interest which is felt in the success of the institution, an interest which the Council feel confident will extend and fructify, as the importance of an extended knowledge of Chemical Science is more generally understood."

With the completion of the Laboratories, the difficulties of the College commenced. A large debt was incurred, without immediate means of payment, for the Building Fund never attained the point requisite to discharge the debt due to the Builder and Architect; while the impatience of some of the Members, whose anticipations of a more early development of the advantages of the School had yet to be realized, induced them to withdraw their support at the moment when a steady adherence to the College was of most vital importance. Although much forbearance was exercised on the part of the chief creditor of the College, the Council felt the necessity of withdrawing the Institution from the danger which threatened it, and at considerable personal sacrifice happily succeeded in this object.

The extracts that follow, from the Report of 1848, will explain the extent of the difficulty, and the mode in which it was met by the Governing Body.

## EXTRACTS FROM THE SECOND REPORT OF THE COUNCIL. JUNE 1848.

"The Council of the Royal College of Chemistry, in making this their Annual Report to the Subscribers and the Public, of the working of the Institution, beg leave to draw attention to the great difficulties by which they have been surrounded during the past year; and if they have, to a great extent, extricated the College from a debt that threatened its very existence, they feel that the Members will give them credit for the personal sacrifice by which this object has been accomplished.

"Before entering into those details, which it will be necessary to do with some attention, in order to explain the peculiar difficulties of their position, they would direct the notice of the meeting to the state of the School. From the first Session to the present, the pupils have progressively increased, and the receipts of the College from students' fees have gone on increasing in like proportion.

"The Council, therefore, confidently hope that in a very few years the Institution will become a self-supporting one, and that the diffusion of Chemical Science, by the education of so many ardent and intelligent young men, will be considered an ample return to the supporters of the College, for the funds they have already contributed to maintain its efficiency.

"It will be recollected that, at the very commencement, it was absolutely essential to the existence of the College, to incur the responsibility of a heavy debt, in building Laboratories and furnishing them with apparatus for the extended practical instruction it was necessary to offer to students; a building-fund was opened for this purpose, and contributions at first flowed in with great liberality; but long before the buildings

were completed, the current slackened, and at last a debt of £2,112 remained, without apparent means of defraying it. At the same time the ordinary expenditure of the Institution exceeded the income on the general account. The annual subscriptions declined, and notwithstanding the increased receipts from the fees of students, the Council became more and more embarrassed for the means necessary to carry out the noble work so well begun. At length the Council determined, as far as in them lay, to do their duty to the members, and they proposed a *pro rata* contribution among themselves, towards extinguishing the debt.

"The Council consisted of thirty-six members, and including some of the Vice-Presidents, twenty-eight noblemen and gentlemen contributed £50 each, either as a gift or loan, to this object.*

"There is a subject which the Council approach with pain and difficulty, viz., the falling off of the subscriptions to the

* The following are the Noblemen and Gentlemen who have contributed £50 each:

| | |
|---|---|
| The Earl of Clarendon. | Niel Arnott, M.D. |
| The Earl of Ducie. | John Raymond Barker, Esq. |
| The Earl of Essex. | John Dalrymple, Esq. |
| The Earl of Ellesmere. | Henry Daniell, M.D. |
| The Earl of Harrowby. | James Adam Gordon, Esq. |
| The Right Hon. Lord Ashburton. | Charles Aston Key, Esq. |
| The Right Hon. the Viscount Hill. | George Lowe, Esq. |
| Viscount Ebrington. | Arthur Marshall, Esq. |
| Viscount Newry and Morne. | James Garth Marshall, Esq. M.P. |
| Sir Josiah John Guest, Bart. | Atkinson Morley, Esq. |
| Sir James Clark, Bart. | Robert Porrett, Esq. |
| William Beckett, Esq., M.P. | George Rushout, Esq., M.P. |
| Richard Blakemore, Esq., M.P. | James Thomson, Esq. |
| Benjamin Bond Cabbell, Esq., M.P. | William Tite, Esq. |

College. The political agitation of the year 1845-6, and the monetary crisis of 1847, have been especially adverse to the raising of supplies towards the maintenance of the College. On every side the public have felt the necessity of economy, and whilst enforced expenditure has met with inadequate returns, and universal charity for the relief of domestic calamities has exhausted their means, the claims of the College to public support, as a measure for increasing the prosperity of the arts, manufactures, and agriculture, have been overlooked or forgotten. There are, however, some of the former supporters who ascribe the falling off of the funds to the non-fulfilment of promises held out in the original proposals for the establishment of the School, and in the early Prospectus of the College. The Council have no desire to avoid this subject; they deem it due to the subscribers, and just to themselves, to state that the sums at their command have never permitted them to carry out what was originally promised as privileges of members. The fact of the Council having already defrayed, from their own resources, a debt of £1,400 incurred in building the Laboratories, speaks for itself. The majority of that body have not shrunk from the responsibility of their position, and it would be unjust to attribute to errors of management the failure of some of the personal privileges of members, when it will be clearly seen that it would have involved an expense they have not had the means to meet, and which would, like the other debts, have had to be borne by themselves alone.

"One of the objects of the College, which, in its very commencement, it was thought possible to carry out, was the analysis of matters sent by subscribers. This, hitherto, it has been impossible to accomplish for the following reasons: 1. The time of the Professor, and his assistants, has been

fully occupied in the laborious and increasing duties of a flourishing school. 2. The want of space, in the Laboratories already erected, to carry on such operations, and the inadequacy of funds for further building. 3. The total want of means for paying such a staff of able and experienced officers, as would have been necessary to give value to analyses so undertaken. Thus the failure in the fulfilment of this design, though attributable to causes not under the control of the Council, has, it is believed, given dissatisfaction to the subscribers, and caused the withdrawal of some support. This is unquestionably a matter of regret to the Council, but they cannot admit that it affords just grounds of blame. Until the public recognize the absolute importance of maintaining in its full efficiency a school that has already completed the chemical education of so many intelligent young men, and that has aided so materially in advancing the science in this kingdom, it is in vain to hold out prospects of personal or private advantage to the subscribers. It is hoped, therefore, that there will be found many to support the Royal College of Chemistry as a great educational establishment, and, that knowing the wide influence chemical science has over our domestic prosperity, they will see that it is only by concentrating our efforts in teaching the more improved modes of analysis, and extending our researches in every department of this extensive field of knowledge, that England can rival foreign nations, and become independent of them for various materials of our domestic trade which we now require to import. Impressed with these feelings, the Council have, at a Meeting held in May last, reviewed the future prospects of the College, and, after much serious discussion, agreed to the following resolutions, to be submitted to the approval of the present General Meeting of Members.

*Resolutions adopted at a Meeting of Council of the Royal College of Chemistry, held on Wednesday, May 10th,* 1848.

1st. That the principal object contemplated in the foundation of the Royal College of Chemistry is, by means of practical instruction in the laboratories and by lectures, and also by researches to advance the science.

Resolved, therefore, that the operations of this institution be strictly confined to these purposes.

2nd. That inasmuch as the expenditure of the College has hitherto exceeded the income derivable from the fees of students, and the annual contributions of subscribers, it is desirable to reduce this expenditure by every economy that does not impair the efficiency of the School; and this may probably be best done by confining the operations of the College to the laboratories, and the area behind the house.

3rd. That it appears, by a careful calculation of the expenditure of the College, that £1,000 per annum will be sufficient to carry on the School; and a reference to the receipts of students' fees for the last two years shows that the Council may calculate upon at least £650 a year from this source, in furtherance of this object.

4th. That in order to obtain the sum of £400, by subscription, the balance required to provide for the necessary annual costs of the School, a statement of the present condition and prospects of the College, be circulated amongst the members and friends of the institution.

5th. That the building fund be kept open for the purpose of receiving contributions to raise a lecture-room, on the foundations already prepared behind the present laboratories, in order to render the Institution, in every way, a complete School of Chemistry.

"Taking these resolutions as a basis, the Council are prepared to advise the re-constitution of the College in the following manner.

"To reduce the annual expenditure, by confining as much as possible the operations of the College to the Laboratories and the area behind the house, and to restrict the business of the College to the extension of the School, as the most important part of the original design; prosecuting such researches as may become of public benefit, and tend to the general advancement of this increasingly important science.

"In consequence of the financial difficulties that have beset the Council, they feel it impossible to promise personal privileges to the members, such as the analysis of subjects of private interest; but as far as their means will allow, they will not shut out, as they have never yet done, investigations of public or national importance. Many such have been undertaken, and executed, in a manner that only makes the Council regret that more could not have been perfected; they look forward, however, with confidence to the future extension of this department of the Institution.

The spirit that animates the gentlemen who have been, and are now being educated in the College, their grateful feeling towards the Professor and his assistants, speak everything in proof of the estimation in which they hold an Institution so perfect as a school, and so ably conducted as it has been by Dr. Hofmann.

"The Council earnestly hope they shall not be deprived of the support of the Members and their friends, in the maintenance of so promising an Institution; and that by limiting their views to the operations of the School, they may provide for the permanent existence of the College.

"The Council believe the time is not far distant, when the

increasing reputation of the College, as a scientific establishment of the highest order, will enable them to support the annual expenditure from the fees of students alone, in which case the subscriptions, they hope to receive, will legitimately form a fund for the erection of a lecture-room, and for extending researches in the science, as originally proposed; but they have determined not to incur, a second time, the responsibility of a building debt, until the whole money, necessary to complete such premises, shall have been collected and deposited in the hands of the Bankers of the College."

The above resolution was proposed and adopted at the General Meeting of members, held June 7, 1848; and the Council are now in a position to announce, that the house in Hanover Square, belonging to the College, which had hitherto been a heavy burthen, not adequately met by the income of the Institution, has been let to a most unexceptionable tenant. The relief to the overburthened funds of the College, thus obtained, will enable the Council to reduce the total expenditure of the Laboratories, and other incidental outlays, to about £1200 per annum; and as the fees received from pupils, it is estimated, will, during the ensuing year, produce from £900 to £1000, there is reason to believe the income, from this source alone, will, in a few years more, cover the whole expenditure of the Institution. The Council, therefore, trust, that the liberality of the scientific public, and of those interested in the wide spread of Practical Chemistry, will enable them to maintain the College in all its originally contemplated usefulness, during the short period of its dependance on external aid. Already the Royal College of Chemistry has attained an extended reputation as a School of high Practical Science, and applications are not unfrequently made to the Professor for men educated in the Institution to superintend

Chemical Establishments elsewhere; and the demand for Practical Chemists will no doubt rapidly increase in proportion as the value of Chemistry, as a means of improving our Arts and Manufactures, becomes more generally known and appreciated.

It may indeed be mentioned, that the College has already supplied assistants to various practical establishments. No fewer than eight pupils have obtained appointments with good salaries; and several others have been offered, but declined.

The satisfactory progress of the School will be traced in the Report of the Professor, Dr. Hofmann; while the elaborate papers upon various subjects of original research, will not only demonstrate the benefits conferred upon science, abstractedly considered, but the kind of instruction given, and the talent, industry, and knowledge displayed in the School.

The pages which follow will amply redeem the pledges originally made to extend the domain of Chemistry, while they encourage the expectation that many useful discoveries await the labours of inquirers, and that not only our manufactures, but agriculture, medicine, and the collateral sciences, mainly dependent upon Chemistry for their future progress, will receive an impulse from the investigations conducted in the Laboratories of the College.

The Council, therefore, refer with much satisfaction to the papers upon various chemical subjects that have emanated from this School; and they hope that the publications of each succeeding year will confirm the value of an Institution, projected at a period most unfavourable for obtaining pecuniary support from the public, sustained during great difficulties, more by individual exertion than by general support, and, at length, it is hoped, established on a secure basis.

The School has continued to advance with increasing prosperity from its commencement.

The Council having compared the amount of the admission fees of students with the costs of the Laboratory, and finding that, however economically managed, each student's education cost considerably more than he paid, resolved to raise the terms from £12 to £15 each session. They have the satisfaction to state, that so far as the experiment has been tried, it has been perfectly successful, inasmuch as not only have the numbers not fallen off, but the working days of the students have been much augmented.

The following Table shews the progress of the school since its commencement.

| | | No. of Pupils. | Income derived from fees. £. | s. | d. |
|---|---|---|---|---|---|
| First year . | Winter session | 26 | 215 | 4 | 0 |
| | Summer session | 37 | 314 | 10 | 0 |
| Second year. | Winter session | 46 | 330 | 0 | 0 |
| | Summer session | 43 | 321 | 10 | 0 |
| Third year . | Winter session | 43 | 298 | 10 | 0 |
| | Summer session | 54 | 439 | 0 | 0 |
| Fourth year. | Winter session | 47 | 500 | 2 | 0 |

It will be remarked, as a satisfactory circumstance, that the amount of fees increases in a greater ratio than the number of pupils; this arises from the proportion of pupils attending during the whole week having augmented, as the subjoined table of the two last winter sessions will show.

WINTER SESSIONS.

| | | 1847. | 1848. |
|---|---|---|---|
| Students working | 6 days in the week | 36 days | 90 days |
| „ „ | 4 days „ „ | 12 „ | 28 „ |
| „ „ | 3 days „ „ | 45 „ | 33 „ |
| „ „ | 2 days „ „ | 16 „ | 14 „ |
| „ „ | 1 day „ „ | 8 „ | 3 „ |
| 40 Students working each week | (1847) | 117 days | |
| 43 „ „ „ | (1848) . . . . | | 168 days. |

The Council beg to repeat the closing paragraph of the Report of 1848, to which they would particularly refer, (the Report having been already generally circulated amongst the Members) as announcing the great remaining object they have yet in view, viz., *the erection of a suitable Theatre for the delivery of lectures, and the assembling of the Members.* The inconvenience of the present temporary lecture-room (while it occupies a part of the Laboratory space destined for other purposes) are such as to prevent the development of the School in that direction. A good lecture-room is alone wanting to render the Institution complete as a College of Chemistry. An additional use of such a theatre would be for meetings of the members, and where lectures during the London season might be given by the Professor on the more recent and important discoveries in Chemistry, and the application of the Science to Agriculture and the Arts, &c.

The Council have ascertained that the estimated expense of building and fitting up a theatre, capable of containing two hundred pupils, with the addition of apparatus, &c., for illustrating the lectures, would be £1800. With such an addition

to the present buildings, the Council feel confident that the income arising from pupils would render the College at once an independent Institution, and they cannot believe that a sum so small, compared to the amount of benefit to the country, arising from a wide diffusion of Chemical Science can long be wanting.

The importance to this country of a more general acquaintance with chemical science and its applications, can scarcely be over estimated. It has indeed become a necessity to our manufacturers to enable them to compete successfully with other states, now cultivating chemistry with the utmost ardour, and availing themselves of its applications to the improvement of their arts and manufactures with the greatest ingenuity. Capital, which has been the boast of this country, can do much, but capital, directed by the lights of science, may accomplish much more; and those nations who neglect to call in its aid, will, to use the prophetic words of the venerable *Humboldt*, "infallibly see their prosperity diminish in proportion as neighbouring countries become strengthened and invigorated under the general influence of arts and science." But the Council deem it unnecessary to dwell upon this subject, as the value of Chemistry is clearly shown, and its applications well illustrated by references to some of our more important manufactures, in an address delivered by Professor Hofmann at one of the evening meetings of the College, and printed in the present volume.

It now only remains for the Council to explain the mechanism of the school; the remaining portion of the volume being assigned to the Professor.

## REGULATIONS REGARDING ATTENDANCE, FEES, &c.

The Collegiate year is divided into two Sessions, each of twenty weeks; the Winter Session commencing in the first week of October, and terminating at the end of February; the Summer Session beginning in the second week of March, and ending with the month of July.

The attendance in the Laboratories is from nine in the morning till five in the afternoon, except on Saturdays, when they close at two o'clock.

Lectures are given by the Professor three times a week, and it is contemplated to increase the number.

The Professor has a number of assistants proportioned to that of pupils. At present there are five; three assistants, and two sub-assistants. The regular assistants are selected from among the more advanced and talented pupils of the school; the junior succeeding the senior assistants when the latter leave the Institution.

The amount of fee paid by each pupil is regulated by the time he works in the Laboratory. The following is the scale of fees:

| | | | |
|---|---|---|---|
| For Students working | | every day during the Session | £15 |
| „ | „ | Four days in the week . | £12 |
| „ | „ | Three days . . . | £10 |
| „ | „ | Two days . . . | £7 |
| „ | „ | One day . . . . | £5 |

This distribution of time and fees is found very beneficial to many pupils engaged in attending to other branches of instruction, or otherwise occupied.

When the pupil leaves the College, he receives a *Certificate*

*of Attendance*,* stating the length of time he has been a laboratory pupil, and specifying the number of days, weekly, on which he has worked in the Laboratories. If his skill in chemical analysis is of a sufficiently high order, he receives also a "TESTIMONIAL OF PROFICIENCY." To entitle a pupil to this honorary testimonial, he must have conducted one original chemical investigation, at least, in the Laboratory of the College, and which has been deemed worthy of publication in the transactions of the Chemical Society of London, and in the publications of the College. A pupil who has received this testimonial, is considered capable of conducting a series of chemical analyses.

* Certificates of attendance at the College are received by the University of London for degrees in Arts and Medicine.

# REMARKS

ON THE

## IMPORTANCE OF CULTIVATING

# EXPERIMENTAL SCIENCE

IN A NATIONAL POINT OF VIEW.

BY

PROFESSOR HOFMANN.

(The substance of a lecture delivered at one of the evening meetings of the College.)

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THE present century, so rich in discoveries in every department of science, is more especially remarkable for the amount of human activity displayed, and the success attained in improvements of all the material interests of society. The rapidity with which we are advancing in this direction is truly astonishing. Every year is fertile in discoveries in science, and almost every day brings forth some new and useful application of it to the purposes of life. Industry is in a state of perpetual advancement; arts and manufactures, which were supposed to have attained perfection, have been entirely superseded by the discovery of new principles, and the introduction of new methods founded on them. It may, indeed, be safely affirmed, that in no previous period in the history of the world has every branch of human industry undergone so thorough a revolution as that which has been effected during the last fifty years.

Take, as an example, the application of *Steam*, as exhibited in the steam-boats crowding our rivers, and traversing the ocean from hemisphere to hemisphere; or in the railway locomotive shooting through the country in all directions, with a rapidity deemed impossible but a few years ago; add to this the impulse given to the arts and manufactures in which this new moving power has been substituted for the uncertain operation of water, or for the employment of animal force, and we need not go farther in search of instances to show the rapid progress of improvement. This we owe to science. The application of steam is the result of the laborious scrutiny of the laws of heat, a department of research which seemed scarcely to promise any fruits of utility, yet whose practical applications, in almost all the arts of life, might now fill volumes of illustration.

Investigations in *Electricity* have been followed by results no less remarkable, and yet the experiments of Franklin, to those who first witnessed them, appeared an idle and profitless occupation; and the elementary experiments of Galvani and Volta, simple as they were, gave rise to the discoveries of Davy, which formed a new era in science. Nor has our knowledge increased more rapidly than have our technical appliances been multiplied; for such is the mental activity of the present age, that scarcely is a new principle established—a new fact added to the stock of our knowledge—but it is straightway made subservient to some useful purposes: witness the improved processes to which electricity has given rise in metallurgy, in the art of silvering and gilding, in the reproduction of artistic objects of every description, &c. But these are trifling advantages, compared to its influence on all the interests of every-day life, as a vehicle conveying our thoughts with the velocity of their conception over continents and under seas. And yet

these are only a few of the more valuable results obtained from the cultivation of pure science. The recent beautiful discoveries of Faraday give intimation of what may still be expected from the labours of philosophers in this department of research. These discoveries are at present of a purely scientific interest; future generations however, will doubtless contemplate them with admiration in practical results, rivalling the most brilliant triumphs of science, realized in our own time.

Scarcely less rich and interesting are our acquisitions from the assiduous inquiries into the nature of *Light*. To the comprehension of its laws, we are indebted for the perfection of the instruments, which, embracing as it were the infinite in both directions, have gathered the vastness of the heavens within the sphere of our perception, and expanded to our view the living world in the water-drop. The phenomena of polarization no longer belong exclusively to abstract science; they have taken their place among the adaptations of science to practical life. Aided by the polarizing prism, the navigator may search the seas for the shoals threatening his destruction, and the fisherman follow the movements of his prey through depths impenetrable to his unaided eye. In the hands of Biot, a ray of polarized light became, to the sugar-manufacturer, an index of the amount of saccharine matter contained in his liquors; whilst directed by the genius of a Wheatstone, we have seen it performing the work of a chronometer.*

The method of fixing the picture of the camera obscura, that marvel in the history of science, placed, as it were, on the boundary line between optics and chemistry, naturally leads our consideration to the fruits reaped from *chemical* inquiry. The study of the solar ray led the way to the contrivance of an instrument, which, imitating the structure

* Playfair: on the "Importance of Studying Abstract Science," &c.

of the human eye, presents within a narrow compass a faithful copy of the grandest scenes and of the most fragmentary miniatures of nature and art. To this picture, the fugitive offspring of a passing ray, chemical science has given permanent life. But before this could be accomplished, what thought, what toil was necessary, what a series of researches were required, perfectly unconnected with the final result which nobody could have anticipated. The ley of the soap-boiler had to give up its iodine, the properties of this new element, and its action on various other substances had to be carefully studied; the investigation of sulphur and its oxides had to teach us the existence and the properties of hyposulphurous acid.

Chemistry, the younger sister of physics, embraces a department of phenomena, the knowledge of which has only of late raised it to the rank of an independent science. Little more than half a century has elapsed since chemical knowledge became chemical science; and nevertheless, how manifold are the services which it has rendered in so short a period. It was in the latter half of the last century, that the combined activity of some of the rarest minds, working in various countries, began to spread light over this field of knowledge. The genius, and laborious researches of a Black, a Priestly, a Watt, a Cavendish, in this country, of a Lavoisier in France, and a Scheele in Sweden, aid the foundations of the grand edifice, which has since been raised by the united labours of scientific chemists throughout the world; they were the workers-out of the principles of that enlightened method of interrogating nature, the introduction of which into the arts and manufactures has effected more in the brief space of fifty years, than the immethodical experiments of many previous centuries had achieved. The 'Transmutation of metals,' and the

'*elixir vitæ*,' which had eluded the ardour and the perseverance of the alchemist, became the legacy of the scientific chemist, who searched for the philosopher's stone, not in sowing the metals, not in the fragrance of flowers, nor in the brilliancy of the morning dew, but in the faithful study of nature's phenomena, and in the investigation of her laws throughout creation. Modern chemistry has not attempted to convert lead into gold, but what immense sources of individual and national wealth have been opened since the adoption of its methods has infused new life into every branch of industry! On comparing the acquirements of the present age, our comforts, our sanitary regulations, our means of communication, &c., with the state of things in the last century, it may with truth be said that human life has actually gained in duration, while its enjoyments have been increased a thousand fold. It would be both interesting and useful, did this brief sketch admit of it, to notice the effects of chemical knowledge on the various branches of industry in every department of life. It would be found, that not only every art and every trade, but that every individual had profited by the labours of the chemist.

In taking a brief retrospect of the rapid progress, which the arts and manufactures depending upon chemistry, have made since the beginning of this century, it will be sufficient to direct attention to a few instances. For this purpose we shall select *Sulphuric acid*, *Soda*, and *Coal-gas*, as illustrations.

Sulphuric acid and soda belong to the products of chemical industry, applied on its very largest scale. An eminent philosopher* of our times has expressed the opinion, that the commercial prosperity of a country may be estimated by the amount of sulphuric acid which it produces, and that the

* Liebig: "Familiar Letters on Chemistry," from which some of the following illustrations are taken.

consumption of soda affords a fair criterion of a nation's civilization, inasmuch as soap and glass, of which this alkali forms so essential an ingredient, are inseparably connected with our notions of cleanliness and comfort.

Up to the end of the last century, the method exclusively followed in the production of sulphuric acid, was that of distillation from the sulphate of iron. This method has now been almost entirely superseded by the introduction of a principle altogether new. The sulphur*ous* acid vapours, which are produced in the combustion of sulphur, had been found convertible, under particular conditions, into sulphur*ic* acid, and a careful study of these conditions led to the far more efficient method at present adopted. The rapidly increasing demand for sulphuric acid compelled our manufacturers to make themselves familiar with all the details of this chemical transformation; and to their perseverance and ingenuity we are indebted for a series of great improvements, both in the construction of apparatus, and in the choice of the materials for the formation of this invaluable product,—improvements which have not only facilitated the process itself, but have likewise proved highly beneficial in various other arts.

We are indebted to the sulphuric acid chambers for the beautiful applications of the oxy-hydrogen blow-pipe in uniting lead without the necessity of a solder.

The want of cheaper sources of nitric acid, for the sulphuric acid process, led to the discovery of inexhaustible stores of nitrates in South America, and to a consequent extension of their usefulness. Nitric acid is now exclusively manufactured from American soda-saltpetre*—whilst the application of nitrate of potassa, which has thus become much cheaper, is confined to the production of gunpowder, in the preparation of

* Nitrate of soda.

which enormous sums of money are annually saved ; large quantities of potassa being thus spared for the far more important purposes of agriculture.

The evolution of nitrous fumes, on which the complete oxidation of the sulphur depends, may be produced, from nitric acid or nitrates, in a variety of ways. At one time, manufacturers thought to effect a saving by generating these vapours from nitric acid by the action of starch, or similar vegetal substances, in which case, *oxalic acid* is formed as a secondary product. Of oxalic acid, additional uses were soon found in various arts, especially in calico-printing; and thus a new trade was started, which still flourishes, although no longer connected with the original purpose.

But one of the most striking triumphs, which chemical science has of late accomplished, is the substitution of minerals containing sulphur found in our own country, for the native sulphur of Sicily, which was formerly exclusively employed for making sulphuric acid. The importation of this material being checked by the short-sighted policy of the Neapolitan Government in 1837, the aid of science was sought to point out new sources of sulphur, which should render us independent of the Sicilian monopoly. The activity displayed in this search is testified by the number of patents taken out, about the period alluded to, for the extraction of sulphur from iron pyrites ; and the success which attended it, is evinced by the fact, that although the restrictions on the exportation of sulphur from Sicily have long been removed, a large quantity of sulphur is still manufactured from our native productions by the new processes, to which this arbitrary enactment had forced us to resort. The amount of sulphur imported is still annually decreasing, as the processes for extracting it from our iron and copper pyrites are progressively improved. These minerals occur to some extent in England, but abound in Ireland. During the past

year, 50,000 tons of iron pyrites were imported from Wicklow, one of the poorest counties in Ireland, which thus derives a benefit from her mineral products, a few years ago utterly valueless.*

There are few chemical processes, conducted on a large scale, which have been brought to such a degree of perfection, as that for the production of sulphuric acid. It is not long, since a hundred pounds of sulphur yielded only 120 or 130 lbs. of sulphuric acid. The produce now is from 280 to 300 lbs.: 306 lbs. being the possible quantity theoretically obtainable. And it is not improbable that the process may be still further improved, especially as regards the construction of apparatus. A highly interesting mode of generating sulphuric acid has been pointed out by Mr. Phillips, who observed that spongy platinum has the property of inducing the combination of sulphurous acid and oxygen, in the same manner as it causes the combustion of the hydrogen in Döbereiner's Lamp. The high price of platinum has hitherto prevented an adequate trial of this beautiful process on a large scale; but let Californian plains of platinum be discovered, and we may witness another revolution of this important branch of industry, which to-day boasts of having reached its culminating point.

The remarkable increase of the production of this article, during the last thirty years, is shown by the following table:

QUANTITIES OF SULPHURIC ACID MANUFACTURED IN BRITAIN.
(APPROXIMATELY).

| | |
|---|---|
| 1820 . . . . . | 10,200 tons. |
| 1830 . . . . . | 30,000 „ |
| 1840 . . . . . | 72,000 „ |
| 1848 . . . . . | 90,000 „ |

* I am indebted to Dr. Muspratt for this communication, as well as for the following statistics respecting sulphuric acid, soda, &c.

These vast quantities of sulphuric acid are employed for a great variety of purposes. Being the strongest acid, which we possess, it is employed to disengage all other acids from their saline combinations. Thus, nitric acid, one of the most powerful solvents of metals, and which so recently has received a novel application in the preparation of gun-cotton, is obtained by distilling nitrates with sulphuric acid. In the same manner, the liberation of phosphoric acid depends entirely upon the superior attraction of sulphuric acid to the lime contained in bone-phosphate. Everybody acquainted with agriculture, knows the important practical result, to which the use of the agent in question has conducted us, since Chemistry, in offering her assistance to the farmer, has given rise to more rational views respecting the application of manures. But the agriculturist could not avail himself of sulphuric acid for bone-digesting, in order to obtain his 'super-phosphate of lime,' unless this acid could be procured at the present moderate price. Phosphorus itself is manufactured by the aid of sulphuric acid, which thus ministers to our comforts by substituting the convenient lucifer-matches, for the awkward tinder-boxes of former days. Sulphuric acid, too, plays an important part in numerous other branches of industry. The great improvement in the candle-manufacture—the isolation of stearine from crude-tallow—is effected by its intervention. This acid is also used by the dyer in the preparation of his colours; by the skin-dresser, for opening the pores of the hides previous to the operation of tanning, by the metallurgist, in the new process of refining silver; and by artificers in numerous minor branches. But by far the largest and most constant demand for sulphuric acid is made by the soda-manufacturer. In the manufacture of soda, more sulphuric acid is consumed, than in all its other applications. Sea-salt presents us with

abundance of soda in the form of muriate (chloride of sodium), but it must pass through the state of sulphate before we can obtain it in that of carbonate, which is the article commonly used. To effect this conversion, 100 lbs. of sea-salt require 82 lbs. of sulphuric acid.

The method of converting sea-salt into soda, was discovered in France by Le Blanc towards the end of the last century. After an attentive study of the action of various substances on sulphate of soda at high temperatures, Le Blanc succeeded in preparing artificially a compound, which up to that period, had been procured only from the ashes of certain sea-plants. No discovery in technical chemistry has produced a more beneficial effect on any branch of industry.

Le Blanc's new method soon reached England, but some time elapsed before it was fully appreciated by British manfacturers. The heavy duty upon salt was a serious obstacle to its introduction into this country; besides, it had to fight its way through all the difficulties arising from a deep-rooted prejudice in favour of Scotch kelp, Spanish barilla, and the pot- and pearl-ashes of Russia and America. Mr. James Muspratt, of Liverpool, who in this country was the first to manufacture soda on a large scale, and with signal success, tells us that he could procure no sale for carbonate of soda, prepared from sea-salt, till he had given away large quantities of it to the Lancashire soap-makers. Their eyes were not long closed to the considerable diminution of the labour, time and cost, thus introduced into their trade: all soap-boilers soon called for soda, instead of kelp and barilla, and in a short time the demand for it became so pressing, that it was sent hot in iron carts from the soda-furnaces to the ley-boilers.

Since that period, but especially since the Government was induced to remove the duty upon salt, the production of soda

has been constantly on the increase; soap has ceased to be an article of luxury in which the wealthy alone could indulge, and glass, a material which in ancient days was valued by kings almost as a gem, has now become a necessary of life within the reach of all. What a remarkable contrast between the results thus produced by the enlightened policy of the British Government, and the consequences of the injudicious impost on sulphur dictated by Neapolitan monopoly, and which well-nigh destroyed the commerce of one of the most important provinces of that kingdom.

The following numerical details respecting the importation of several articles, the sale of which has been strikingly affected by the soda trade, may be found interesting.

IMPORTS INTO GREAT BRITAIN OF SULPHUR, BARILLA, POT- AND PEARL-ASHES, AND PALM-OIL.

| | Sulphur. Tons. | Barilla. Tons. | Pot- and Pearl-ash. Barrels. | Palm-oil. Casks. |
|---|---|---|---|---|
| 1820 . . . | 3,434 | 8,594 | 34,226 | 2304 |
| 1830 . . . | 9,409 | 8,474 | 44,878 | 31,204 |
| 1840 . . . | 23,935 | 372 | 17,014 | 41,712 |
| 1848 . . . | 21,442 | none. | 18,546 | 57,997 |

The amount of soap now annually exported from Liverpool alone, considerably exceeds the quantity shipped in any one year from all the ports of England, previously to the conversion of sea-salt into the soda of commerce.

Nor has the influence of the artificial production of soda been confined to the manufacture of soap and glass. An important and flourishing branch of industry, that of bleaching by means of chloride of lime, received a new impulse by the change in the alkali trade. The hydrochloric acid evolved during the conversion of sea-salt, (hydrochlorate of soda), into sulphate of soda, was long allowed to escape as useless; but

when the operation came to be worked on a large scale, the torrents of this gas which were poured into the atmosphere became an annoyance to the neighbourhood. Various methods were devised to obviate this, but without effect; and, the loftiest chimneys failing sometimes to carry off the vapours, it was found necessary to condense and to collect the acid, which is now employed for various useful purposes. When heated with peroxide of manganese, it yielded up its chlorine, which, when combined with lime, forms the common bleaching powder. We were thus so abundantly provided with a portable bleaching agent, that the old and tedious method of bleaching was soon entirely superseded. Here again we owe to chemistry an immense saving both in labour and capital. The influence, which the new bleaching process exercised upon one of the most important branches of British industry, namely, the cotton manufacture, needs no comment.

The preceding sketch gives but a partial view of the vast influence, which the increased production of sulphuric acid and soda has exercised upon our manufactures, but it is sufficient for our present purpose.

Let us now take a glance at the assistance afforded by science in a chemical manufacture, which within the last twenty-five years has become of national importance, viz.: the production of *Coal-gas*.

The evolution in different localities of inflammable gases, from the ground, had been noticed from time immemorial, and the connexion of these gases with deposits of coal had been recognised as early as the middle of the seventeenth century.* Years however elapsed before correct views of the nature of these gases were established by experiment. In 1739, coal was

* Mr. Shirley's experiments on the Burning Well of Wigan, in the Transactions of the Royal Society for 1659.

for the first time subjected to distillation by Dr. Clayton, Dean of Kildare, who thus succeeded in imitating artificially the formation of native gas. From this moment the subject was never lost sight of, but it was not till the end of the last century, that the intellectual impulse of that memorable period overcame the difficulties, opposed to the practical application of this new source of light. These obstacles we know have been at last entirely removed; gas-light is now universal; our streets, our public buildings, our private dwellings are brilliant with its radiance. In our daily enjoyments of its benefits, we have almost ceased to be conscious of the comfort and even personal security, which we owe to this, as yet, best, cheapest, and safest of lights.

But, to the attainment of this end, how many were the scientific problems to be solved, how often had the gas-maker to seek the assistance of the scientific chemist, and to avail himself of the results of his researches, instituted originally perhaps for very different purposes. What a difference between the gas with which Mr. Murdoch lighted up the Soho Foundry in Birmingham, and that now circulating in the arteries of our nightless towns!

The gas produced by the distillation of coal is not an uniform substance. Together with the principal illuminating constituents, light carburetted hydrogen and olefiant gas, many other gases are evolved during the distillation, some of which, e. g. hydrogen, tend rather to diminish the illuminating qualities of the gas, whilst others, as ammonia and sulphuretted hydrogen, are injurious to health. This formed a serious obstacle to the adoption of coal gas as a domestic light. By the aid of chemistry, the composition of coal gas was ascertained, and the nature of its constituents, useful and deleterious, determined. Founded on the knowledge thus obtained, means were devised

for the separation of the latter: the temperature was indicated, at which the purest gas comes over during the process of distillation, whilst for the improvement of gas less rich in illuminating constituents, the beautiful and economical process of naphthalisation was introduced. And finally may be noticed the elegant burners contrived for the safe and economical combustion of the product.

Here again a few figures will aid the conception of the extent, which this branch of industry has attained. In England 6,000,000 tons of coal are annually consumed in the manufacture of gas, at a cost of from £12,000,000 to £15,000,000. In London alone about 400,000 tons of coal are used every year, producing not less than 3,600 millions cubic feet of gas, and 400,000 chaldrons of coke, of which 150,000 are consumed as fuel in the gas works, the remainder passing into the market for general consumption. The length of the mains in London alone is more than 1800 miles, and the number of burners upwards of half a million, while the capital employed exceeds £4,000,000. There is no town in England with more than 4000 inhabitants which does not enjoy the advantages of gas.*

The extent, to which the use of gas has affected the arts and manufactures in this country, can only be conceived by those, who are aware of its innumerable applications in the double capacity of giving heat and light. To our experimental chemists the benefits afforded by gas cannot be overrated, more especially in England, where the price of spirits of wine is so exorbitant. But for the use of gas in the laboratory, the progress of chemistry in this country must have been greatly retarded.

In speaking of the general influence of the manufacture of

* I am indebted to Mr. George Lowe for these statistical facts.

coal gas, it is impossible to leave unnoticed the number of hands daily engaged in raising whole strata of coal, and in loading and navigating the fleets, employed in conveying it, not only to the different ports of this kingdom, but to foreign countries, which consume a larger quantity of English coal for the production of gas than is generally known. The extension of the gas enterprise produced a sensible effect on the iron works by the vast number of retorts, the stupendous gas-holders, and the endless pipes, required for generating, storing, and conveying the gas. Several other branches of trade were also forced into increased activity, and even new trades sprang up in consequence of the extended use of gas. The substances produced in the purification of gas naturally attracted the attention of the gas manufacturer; and chemistry soon pointed out valuable purposes to which they might be applied. The oily matter, which separates as a secondary product in the distillation of coal, yielded, when purified, in its more volatile portion, the most convenient solvent of caoutchouc, another part of it was found to be an efficient preservative of timber, and the pitchy residue formed the chief ingredient of an excellent substitute for the flag-stones of our pavements, while the ammoniacal liquors were found useful in improving the fertility of land. Thus, after the lapse of countless ages, was the nitrogen of petrified fern-forests resuscitated in the ammoniacal liquors of the gas-works, to vegetate once more and increase the produce of our corn-fields.

Having thus given a brief outline of the aid, which chemistry has recently afforded to the manufacture of sulphuric acid, of soda and of gas, as indicative of the rapidity in which British industry has been advancing, we might take a similar survey of the advantages which chemistry, as the true

interpreter of oryctognosy, has conferred on the miner and metallurgist, and of the benefits which geology must derive from the light thrown upon its metamorphoses by chemistry. We might moreover trace the close connection existing between chemistry and pharmacy, and dwell on the important assistance, which the Pharmaceutist is sure to derive from the assiduous cultivation of chemistry, and of which the perception is becoming so general, that I believe the day is not far distant when every "Chemist and Druggist" in England will truly deserve the name of Chemist.

But we must limit ourselves to pointing out a few of the advantages which the most important branch of human industry, Agriculture, owes to our science. At an epoch when the resources of the agriculturist seemed almost exhausted, chemistry offered her hand, to lead him up a new ascent of improvements. An accurate study of the composition of plants, taught us the actual nature of their food,—that it was partly obtained from the atmosphere and partly from the soil. It taught, likewise, that while the nutriment derived from the air—identical for all plants—is continually restored to it by the never-ceasing processes of respiration, combustion, and putrefaction; the mineral aliment—varying with each vegetal species—is drawn from a source which is liable to exhaustion. The knowledge of the importance, to the development of plants, of a due supply of their mineral constituents, implied the recognition of the necessity of faithfully restoring to the soil such inorganic matters as are removed from it in our crops. This principle sealed the pledge of alliance between Agriculture and Chemistry. To keep up the fertility of his fields, the cultivator of the soil had to make himself acquainted with its general composition, and with the nature both of the particular substances, which he is annually extracting from it,

and of those with which he must supply the loss. For each of these purposes, the aid of chemistry became indispensable to the farmer. Davy's excellent work on Agricultural Chemistry first called the attention of the more intelligent British farmers to the value of chemistry in the improvement of their art; but it is only within the last few years that the attention of agriculturists has been generally directed to the subject by late works, more particularly of Liebig and Boussingault. The nature of manures once clearly defined, almost every agricultural improvement, at which practice had arrived by slow degrees, received a satisfactory explanation; whilst a variety of improved applications necessarily suggested themselves. The principles of fallowing, and of the rotation of crops, and the theory of soil-burning, are no longer mysteries; the action of lime, of wood-ashes, and of bones, is now perfectly intelligible. In this country, too high a value cannot be set upon the discovery of new sources of material, convertible by the farmer into human food. Chemistry has put us in possession of the excreted wealth, which centuries had accumulated in the islands of the Pacific; and it is also exerting its influence, through the enterprise of joint stock companies, to prevent the enormous waste of valuable matter perpetually and irrevocably swept away by the Thames, and others of our large rivers, as also to substitute, for natural manure, artificial products, for the components of which the refuse of every trade and manufacture is carefully sifted. Perhaps there is no more striking illustration of the value of the aid, which agriculture has derived from her new ally, than the success which of late has attended the search for *mineral* manures. This search, directed by a philosophical interpretation of a few isolated facts, has been rewarded by the discovery of considerable quantities of phosphate of lime in various

parts of England; thus realizing the prophetic anticipation of Liebig, that, "in the remains of an extinct animal world, England is to find the means of increasing her wealth in agricultural produce, as she has already found the great support of her manufacturing industry in fossil fuel, the preserved matter of primeval forests, the remains of a vegetal world." *

Nor is the increase of his *vegetal* produce the only object in the pursuit of which the farmer relies upon the counsels of the chemist; in the feeding and fattening of his *animal* stock, he stands in no less need of his instruction.

And here we may briefly allude to the benefits, which Physiology, Pathology, and Medicine in general, have derived, and must still further derive, from the prosecution of chemical inquiry. The investigation of the food of plants was followed by a no less vigorous scrutiny of the food of animals. The materials consumed by animals were shown to fulfil two distinct purposes in their economy, enabling us at once to separate into two distinct classes the substances supplying each, respectively,—the aliments of nutrition, and those of respiration. In vegetal fibrin and albumin, we became acquainted with a group of nitrogenous compounds, which we find again in the animal organism as the chief constituents of the blood. These materials, prepared by vegetal life, the herbivorous animal receives and assimilates into its blood, to supply the constituents of its different organs and structures.

Again, we have a series of substances such as fat, sugar, gum, starch, &c., which, though not truly to be called nutriments, as having no part in the construction of the body, are no less essential to the maintenance of life. These substances

* Familiar Letters on Chemistry.

serve the process of respiration; combining with the oxygen inspired by the animal, they continually compensate the loss of temperature, and thus become the source of animal heat. And here presents itself one of the most interesting subjects for contemplation,—the animal organism in its relations to the surrounding atmosphere. The full appreciation of the effect of air and temperature on the animal system, was a most important step towards a true understanding of the conditions of health. A vast number of diseases originate in disturbances of the relation between the living system and these influences, the intimate knowledge of which affords to the physician the simplest, safest, and most efficient means of preserving health and of curing disease.

Valuable as have been the fruits of chemical inquiry, still more may be expected from the further prosecution of this study. The view that the action of most of our medicines is chemical, is daily growing into a general conviction. We admit that, with every change wrought by pharmaceutical agents in the state of our organism, there occurs a corresponding change in its composition, resulting from their reaction on one or more of its constituents. But of these transformations, which doubtless could be expressed in numbers as definitely as can our laboratory processes, how few are we in a condition to explain; in how few instances has the physician even a vague conception of the mode in which any medicine performs its office! Nobody doubts the power, which the principles of the Cinchona-bark, or of tea and coffee, exert upon the living body; but we are perfectly in the dark as to the way in which they act upon the animal economy. But if we meet with a series of similar substances in several animal fluids, *urea* and *creatine*, almost constantly present in urine,

*glycocoll** generally and *cystine*, occasionally excreted in the same liquid, and if we find that all these substances exhibit in their chemical relations a close analogy with *quinine* and *theine*, we begin to feel a sort of anticipation of the manner in which these agents may act upon the system. Such examples illustrate at once the nature of the aid which therapeutics with certainty may expect from the progress of organic chemistry. Medicine some years ago found itself in a predicament very similar to that of agriculture at the same period; its resources appeared to be in a state of exhaustion, the rich capital of facts accumulated in the department of organic morphology by the industry of the anatomist and by the acumen of the physiologist, could not yield its full fruits, until an equivalent of knowledge had been drawn from the study of bio-chemical phenomena. This state of things, however, is rapidly changing; associated with Chemistry, Medicine no longer draws the veil of vitality over processes, the mystery of which may be unlocked by the key of analysis; it no longer shrinks from climbing, step by step, the ladder of recognition, because its upper extremity, disappearing among the clouds, seems to rise for ever beyond the grasp of inquiry. The special zeal, with which the field of organic chemistry has been cultivated during the last twenty-five years, the simple and accurate methods which we now possess for determining the composition of organic products, the amount of analyses actually performed, and, more than all, the still untiring energy of the numerous labourers in the same field of investigation, hold out the promise that the connexion between Medicine and Chemistry, becoming daily more intimate, will be productive of benefits,

* In combination with benzoic acid, as hippuric acid.

the importance of which we can scarcely venture to estimate in the present state of our knowledge.

I have thus endeavoured to indicate some of the most remarkable features of the new field, into which the present generation has been conducted by the study of natural science, and especially of Chemistry. I have tried to sketch the prospects, which a continuation of these labours promises to open before us. My space will not allow me to consider the study of nature under its other equally important aspect, as the unfailing source of the purest and highest intellectual enjoyment, and as a means of mental training, more effectual perhaps than any other discipline. A future opportunity may permit of my following out this subject more minutely. My principal object, on the present occasion, has been to insist upon the importance of cultivating natural science in its bearings upon the whole mechanism of society, as the mainspring both of individual and national prosperity; and I cannot conclude more appropriately, than in the words of the venerable Humboldt, one of the most distinguished philosophers of the present age: "An equal appreciation of all parts of natural know-
" ledge is an especial requirement of the present epoch, in which
" the material wealth, and the increasing prosperity of nations are
" in a great measure based on a more enlightened employment
" of natural products and forces. The most superficial glance
" at the present condition of European states shows, that those
" which linger in the race, cannot hope to escape the partial
" diminution, and perhaps the final annihilation of their
" resources. It is with nations as with nature, which according
" to a happy expression of Goethe, knows no pause in
" increasing movement, development, and production, attach-
" ing a curse to standing still.

"Those states, which remain behind in general industrial "activity, in the selection and preparation of natural substances, "in the application of Mechanics and Chemistry, and in which "a due appreciation of such activity fails to pervade all classes, "must see their prosperity diminish, and that the more "rapidly as neighbouring states are meanwhile advancing, both "in science and in the industrial arts, with, as it were, "renewed and youthful vigour."*

* Cosmos.

# RESEARCHES

CONDUCTED IN THE LABORATORIES

OF THE

# ROYAL COLLEGE OF CHEMISTRY.

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## INTRODUCTION.

In offering for the first time, to the friends and supporters of the College, a detailed account of the experimental studies, which have been conducted in the laboratories, I feel the necessity of a few prefatory remarks in explanation of the nature of researches, which may appear recondite to the general reader, unacquainted with the mechanism of chemical investigation. The greater number of the experiments described in the following pages, have been performed by pupils of the institution, with the view indeed of contributing to the stock of chemical knowledge, but principally with the desire of acquiring practical experience by conducting them. In explanation of this double object, it will be proper to notice briefly the general plan adopted in laboratory instruction, in order to fix more particularly the point of view from which these researches should be regarded.

Chemistry, although embracing as wide a field of inquiry as any of the experimental sciences, differs from most of them in

the uniformity and simplicity of its methods of investigation. Let us for a moment compare the task of the natural philosopher with that of the chemist. Almost for every new line of study, the former has to lay down a new plan of operating; in most cases, indeed, this new mode of proceeding forms the principal part of his labours. This also often occurs to the chemist in his researches, but much more frequently, to attain his object he has only to avail himself of processes, which have been approved by experience, and which, when carried out in the proper manner are sure to lead to correct results.

Again, the natural philosopher must provide for every new inquiry a new series of instruments, often actually to be invented for the occasion, and not unfrequently to be constructed by a skilled artificer, at a considerable expenditure of time and money. On the contrary, the apparatus used by the chemist in the analysis of an almost endless variety of objects, seldom requires much alteration from the simple forms which have been generally adopted; and when changes are necessary, they are for the most part readily contrived with the aid of glass, cork, and caoutchouc.

This dissimilarity in the methods of proceeding sufficiently explains why the study of natural philosophy has always been, and will continue to be, pursued in a different mode from that of chemistry. The student, who by lectures and reading has made himself familiar with the principles of physics, and who, after having mastered the known facts of the science, is himself desirous of adding to them, is thrown upon his own resources, both intellectual and economical. He finds no other teacher except his own ingenuity, and his ultimate success depends in a great measure upon casualties, which are but seldom under his control. Very different is the case of the chemical student,

Possessed of the general facts of the science, he enters the laboratory, where a new field of study opens to him, which when cultivated with zeal and assiduity, promises a rich and early harvest. His own performance of experiments gives him ample opportunities of confirming, of correcting, or extending such parts of his knowledge as may have hitherto remained uncertain, erroneous, or insufficient. Such a method of proceeding is admirably calculated to impress upon the memory the numerous details, a familiarity with which is as important to the student as the knowledge of general principles, and can never be dispensed with. Although availing himself of all the opportunities afforded by lectures and books, the unpractised student finds it impossible to retain, even in the most faithful memory, the peculiar properties of the individual elements and their numerous compounds,—their external appearance, their comportment with reagents, form and colour of the endless variety of precipitates, &c.; but all this can easily be acquired in the actual contact with these substances, by handling them, by hourly witnessing again and again the phenomena arising from their mutual actions. And here presents itself at once another advantage of laboratory instruction. The most perspicuous and minute description of an experiment offered to the student in a manual, does not secure him from a host of difficulties which beset him as soon as he attempts to imitate it. These difficulties, often sufficient to damp the courage of the most persevering learner, and always the source of much loss of time and labour, are readily overcome under the eye of a teacher, by whose experience and friendly advice, the obstacles which seemed insurmountable to the unassisted student, rapidly disappear. A further advantage which the laboratory affords to the practical student is the ample opportunities of witnessing, in a comparatively short time, a vast variety of processes which

are being constantly carried on in an institution consisting of a great number of experimentalists. This is perhaps one of the most important advantages of a public laboratory: the student whose eyes are open to what is passing around him, may derive from the work of his neighbour almost as much benefit as he acquires by his own manipulations.

The fundamental studies of the laboratory are the same for all those who intend to make themselves practically acquainted with analysis. It is only after having, by steady assiduity, become familiar with the principal properties of the elements and their compounds,—after having mastered the most important methods of distinguishing, separating and estimating chemical substances, and having acquired sufficient skill and practice in manipulation, that a higher line of pursuit is selected, which naturally varies with the abilities and with the ultimate object of the individual.

It is usually at this period, that the student, who is willing to proceed farther in the science, chooses a subject for investigation, in which he finds not only opportunities of additional practice, but more particularly of initiating himself into the art of research. At the same time his perseverance is encouraged by the hope of eliciting, by his own exertions, some new facts, either directly applicable to practical purposes, or useful as material for the extension of the science.

There is no want of subjects of research. We have, in fact, an unlimited field before us. The analysis of soils, as the source, and of plant-ashes as constituents of our food; of minerals, in their solid form, or in solutions as "mineral" waters, in the ores, as well as in the metals of the smelter, and in all the other products of manufacturing industry, presents a sufficiency of subjects, full of interest for the pupil, and worthy of the study of the adept. Again, we possess, in the depart-

ment of Organic Chemistry, a boundless territory of research for the solution both of purely scientific theorems and of problems of practical application.

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The following papers embrace a variety of subjects, which, in order to retain a long established classification, have been arranged in two distinct series: namely, researches in Inorganic and Organic Chemistry.

Respecting the investigations belonging to the former class, I need not enter into many details. They comprise analyses of waters, of plant-ashes, and of products of industry. The object of analyses of this kind is intelligible even to persons possessing a limited knowledge of Chemistry.

The effect of a mineral water is no longer ascribed to the vital power of the spring, nor to some mysterious agent far too spiritual for the grasp of ordinary inquiry. Everybody now knows, that it is due to the presence of certain mineral constituents, the nature and quantity of which may be easily ascertained by the chemist. The composition of a water once known, there is no longer any difficulty in reproducing it with all its qualities,—a fact sufficiently established by the extensive manufacture of mineral waters now conducted in almost every country. The artificial imitation, however, of a natural water from a good analysis, is by no means the ultimate object of the chemist, in ascertaining its composition. A mineral spring contains certain active constituents, to which the effect observed by the physician is due; whilst the presence of others, far from enhancing, may even tend to diminish it. If we were able to distinguish the constituents actually efficient in any case, we could doubtless prepare a much more active composition than the native water itself. Now, although we possess already a very considerable number of

analyses of medicinal springs, the physician has, as yet, by no means a perfectly correct conception of the physiological effect due to the individual constituents of any one of them. A knowledge of this kind, certainly, is very difficult to be acquired; being, indeed, accessible only through a careful comparison of the influence upon the animal economy, of waters differing in their composition. For this purpose, however, their composition must be comparable: the results of all the analyses should be arranged on one principle, whatever this principle may be. It is, perhaps, chiefly in consequence of a want of uniformity in arrangement, which renders our older analyses unsuited for such comparison, that our knowledge has not advanced farther in this direction.

The analyses of the Thermal Spring of Bath, by Messrs. Galloway and Merck, and of some of the Cheltenham Waters, by Messrs. Abel and Rowney, are the first of a series intended to be conducted in the Laboratory of the College, so as to embrace gradually all the more important mineral waters of Great Britain.

Closely connected with this investigation are the analyses of the Artesian Well in Trafalgar Square, and of the Thames Water. The value of these researches will be at once appreciated, if we recollect that a knowledge of the composition of these waters is not only important for the great variety of economic purposes for which they are daily employed in the metropolis, but also in connection with a question which has lately attracted public attention. Everybody is aware of the danger attending the use of leaden pipes, for conveying and distributing waters. Experience has taught us, that while certain waters may be safely conducted through such pipes, others act almost immediately upon the metal, the oxide of which is soluble to a certain extent. We are indebted for some

beautiful experiments upon this subject to Christison, R. Phillips and Col. Yorke; we know, indeed, that the behaviour of water with lead depends chiefly upon its mineral ingredients, that very pure waters act much more rapidly than those containing saline substances, and that the presence of salts, in a certain quantity, altogether prevents this action. But here, again, we have by no means arrived at a perfectly distinct knowledge respecting the influence due to the several compounds dissolved. A very great number of experiments is still wanting to enable us to pronounce, from the analysis of a water, the safety, or the danger, of conducting it through leaden pipes.

The next paper, on the analysis of the Ashes of the Orange Tree, by Messrs. How and Rowney, though of limited practical utility, has considerable interest for the inquirer in Vegetal Physiology; being, in fact, one of the first researches in which the mineral constituents of the *different* parts of the *same* plant have been accurately ascertained.

The papers on Inorganic subjects conclude with an analysis, by Mr. Rowney, of the variety of Bohemian Glass of which combustion-tubes are manufactured. The present mode of determining the composition of organic compounds, consists in burning them in tubes of glass, and collecting the products of combustion in appropriate apparatus. The substance of which the tubes employed for this purpose are composed, is a very tough potassa-glass, exclusively manufactured in Bohemia; and it was a matter of some surprise, that the composition of a material, which has contributed in so remarkable a manner to the progress of Organic Chemistry, should not have attracted more general attention among chemists.

The series of papers on subjects of Organic Chemistry opens with a beautiful and elaborate research by Mr. Warren De La Rue, on the Colouring Matter of Cochineal. Among the various

substances used for dying, few are of so high an interest as the cochineal; which, long considered as the berry of a plant, is now well known to be an insect belonging to the family of *Coccus*. In the analysis of cochineal, an entire animal organism presenting itself to the investigation, the separation of its pure colouring principle was necessarily attended with unusual difficulties. Mr. De La Rue succeeded, for the first time, in obtaining the colouring matter of cochineal in a state of chemical purity; he proved, by decisive experiments, that this substance, which he describes under the name of carminic acid, is free from nitrogen, (which element had been asserted to be present by Pelletier), and that the powerful reactions attributed to this weakly acid compound, were due to the presence of phosphoric acid, liberated in the processes of former inquirers. The Memoir of Mr. De La Rue, which has gained him the approbation of a very eminent critic,* contains besides a very accurate account of the colouring matter itself, a detailed description of several of the other principles occurring in the insect, and of various interesting products arising from its decomposition.

The two next papers, on Cumarine, by Mr. Bleibtreu, and on Caffeine, by Mr. Nicholson, are devoted to the examination of two crystalline principles, formed in the process of vegetation, the one in the *Asperula Odorata*, the other in the coffee-shrub.

The former plant being extensively employed in Germany in preparing the favourite *Maiwein* (Maywine) of that country, has been the subject of several examinations, some of which have shown the presence of benzoic acid, whilst others appeared to prove that its active principle is cumarine, found in the Tonka-bean. The experiments of Mr. Bleibtreu leave no

* Vide Liebig's Annalen, vol. LXIV, p. 39.

doubt respecting the absolute identity of the principles of the tonka-bean and of the asperula.

More generally known is the substance, which formed the subject of Mr. Nicholson's experiments. Caffeine, a beautiful crystalline compound, discovered in the coffee-bean by Runge, and subsequently analysed by Pfaff and Liebig, has an interest peculiarly its own, as being among the active constituents of one of our most common beverages. Additional interest, however, was attached to this substance by the later discovery, that it likewise occurs in the tea-plant, and in the *Guarana Officinalis*, a decoction of which is extensively used in the Brazils as a medicinal drink. The essential principle of these plants, (which has since also been found in the Paraguay tea-plant), originally described under the name of theine and guaranine, a more minute analysis has proved to be identical with caffeine, thus demonstrating, the certainly remarkable fact, that four distinct plants, independently selected in entirely different parts of the world, for the preparation of domestic beverages, are characterised by the same prominent chemical constituent, which hitherto has not been met with in any other plant. The composition assigned to caffeine, by former inquirers, and more particularly of late by Dr. Stenhouse, has been declared incorrect by M. Payen, of the French Institute; but Mr. Nicholson proved, by a large number of very decisive analyses, the utter inadmissibility of the new formula proposed for caffeine by Payen, and thus established the accuracy of the original analysis.

The preceding organic investigations, although chiefly interesting in a scientific view, are nevertheless in some points directly linked with practical utility. It is evident that in extracting and preparing so delicate and precious a colouring matter as carmine, we should be intimately acquainted with

the chemical properties of its constituents, in order to avoid all sources of loss in the manufacturing process, and all reactions which, in its application, might possibly injure the brilliancy of the colour.* Nor can it be doubted, that if there is any hope of ever ascertaining the mode in which the action of vegetal principles, such as cumarine and caffeine, is exerted on the animal economy, the first steps towards this recognition must be an accurate knowledge of their chemical composition and properties.

It will be perhaps more difficult to point out the interest attached to the succeeding researches. I allude to some investigations on the volatile organic bases, chiefly on aniline, containing a minute description of a considerable number of substances produced by the action on it of various chemical agents. Again we find a series of papers by Messrs. Abel, Field, Nicholson, and Noad, chiefly devoted to the investigation of the constituents of cumine-oil, and of the metamorphoses which these compounds pass through under the influence of certain chemical processes. Now I am fully prepared to hear the question:—what is the use of all these products?—Aniline, cyaniline, iodaniline, melaniline, cumidine, and other even less pronounceable ——ines of similar construction, cuminamide, cumol, cymol, toluol, toluylic acid—what do these substances mean? Has any one of them received practical application? Have they been found useful in the arts, in medicine, &c.? I readily confess, that none of these compounds have as yet found their way into any of the various appliances of life. We have not been able to use them for dying calico nor for curing disease; nevertheless, I may succeed perhaps in

* It is a well-known fact, that many dyers purchase advantageously the cochineal that has been incompletely exhausted by unskilful operators in the same business.

reconciling some of our friends to the study of the apparently abstract theorems, in the solution of which the production of these substances is involved.

Let me first of all remind them of some actual benefits which studies of a similar nature have conferred upon society, studies not more evidently connected with practical questions, than those to which I have above alluded. In inorganic chemistry, we possess indeed a great number of familiar instances of this kind. We may allude to the artificial reproduction of the *lapis lazuli* (ultramarine) by Gmelin, to Fremy's successful imitation of the old Venetian aventurine glass, to the manufacture of artificial cements, greatly excelling those offered by nature, or to the happy substitution of the stable and innocuous oxide of zinc, as a pigment, for white lead, which is so easily injured, and so frequently gives rise to serious diseases. Again, we have the introduction, by Berthold and Bunsen, of peroxide of iron as an antidote to arsenic, and by Melsens, of iodide of potassium, as a remedial agent in cases of poisoning by lead and mercury ; and more particularly the splendid researches of Professor Graham, on the phosphates, which, purely scientific in their conception, are becoming important to the physiologist and the medical man, by throwing light on some of the most recondite processes of the animal economy.

Nor have researches in Organic Chemistry been unproductive of valuable practical results.

The knowledge of chloroform and of perchloride of carbon, was the result of purely scientific investigation. When, by the researches of Dumas, Liebig, and Regnault, we first became acquainted with these substances, the names of which are now in everybody's mouth, they were appreciated only by the chemical inquirer. And yet, scarcely had a new necessity been created by the discovery of the anæsthetic properties of ether,

when these compounds rose at once into universal estimation, as medicinal agents depriving of their terrors some of the most awful conditions of mental and bodily anguish to which humanity is subjected. The sources of chloroform and perchloride of carbon being multiplied, and the processes for their preparation having been improved in consequence of the increased demand for these substances, their greater accessibility did not fail to suggest new purposes for their application. We may notice here the use of chloroform as a solvent, both for the purposes of chemistry and of industry, and the action of this compound, distinguished equally by its volatility and by its incombustibility, in the 'combined vapour-engine'; although we cannot share the sanguine expectations of the inventors of this interesting contrivance.

Again, to pass from great to small things, gun-cotton, of ephemeral celebrity, at one time threatening the destruction of our race, but now tamed down into an ethereal solution (collodion) for the preservation of our cuticle, is the offspring of purely scientific research. It was in order to unravel the molecular construction of organic bodies, that chemists were led to investigate the action of oxidising agents, especially of nitric acid, on these substances. These endeavours materially assisted in the elaboration of Dumas' substitution theory, which, in gun-cotton and collodion, has stepped from the regions of speculation, into the thoroughfares of life.

The minute chemical investigation of the complex product, which we collect in the distillation of wood, has introduced to us a series of bodies, which when discovered, were interesting only to men of science. But how soon did these substances assume a practical value! The largest quantity of acetic acid used in the arts and manufactures, is now obtained from the above source. The pyroxylic spirit also, generated in the same process, is now extensively used instead of alcohol, both as a

solvent and as a fuel; and thus large quantities of corn, sugar, and potatoes (formerly devoted to the mash-tub of the distiller) are saved for their appropriate destination, the nutriment of man. Again we have found in creosote a valuable remedy in some diseases; and finally, we possess in paraffine a substance, which, known for years in laboratories as a chemical curiosity only, promises to acquire an unexpected importance, since the possibility of obtaining large quantities of it, in the distillation of Irish peat, appears to point it out as a substitute for stearine. Indeed, the actual formation of a company is likely to realize its advantages in the candle trade.

We might go on for hours instancing benefits of a similar kind derived from purely scientific investigations. Some of Liebig's latest researches have been particularly happy in this respect, both in explaining the nature of some of the most familiar processes of domestic life, and in pointing out new methods and applications, which, as the preparation of portable soup, e. g., may gradually, and especially in this country, become important even in a commercial point of view.* But I must refrain from entering into further details, in order to leave room for a few remarks on another important department of our subject.

One of the most interesting results of the study of organic metamorphoses, with which we have become acquainted during the last twenty years, is the artificial formation in the laboratory, of substances formerly generated by direct vital processes exclusively. We now reproduce artificially the fragrance of the meadow sweet (*spiræa ulmaria*) by treating the salicine of the willow-bark with oxidising agents; by exposing fusel-oil, the fetid intruder of vinous fermentation, to the same action, we have succeeded in procuring the acid peculiar to the *valeriana*

* Liebig: "Researches on the Chemistry of Food," &c.; London, Taylor and Walton.

*officinalis*, whilst the fatty acids occurring in butter have been obtained in the decomposition of sugar, and this again we have seen produced from starch, and even from woody fibre. Allantoin, the crystalline principle in the allantoic fluid of the cow, has resulted in the oxidation of uric acid; and as soon as wintergreen oil, the volatile essence of the *gaultheria procumbens*, had been carefully studied as to its composition and properties, its artificial formation in the hands of the chemist followed, as it were, of course.

These instances may, however, appear trifling in comparison with some of the more recent achievements of Organic Chemistry. In the examples given above, we certainly obtain by artificial processes, substances which also occur as products of vitality. But before we can reach them, we still must avail ourselves, although indirectly, of the assistance of the living organism; e. g., for the preparation of the oils of the spiræa ulmaria, and the gaultheria procumbens, the salicine of the willow-bark is required; and the acids of the valeriana, and of butter, cannot be obtained without the aid of sugar. Chemistry, however, in its rapid rise, has actually succeeded in building up, from their elementary constituents, a variety of compounds, which either really occur in living organisms, or were formerly exclusively obtained by their assistance,—thus removing, gradually, the barrier which had hitherto separated organic and inorganic nature. Cyanogen is no longer known only as a product of the decomposition of organic matter, we have learned, that, at high temperatures, carbon and nitrogen may be combined, in the presence of an alkali, to form cyanogen. Under the influence of water, cyanogen gives rise to the formation of ammonia, the general product of the putrefaction and distillation of nitrogenous organic substances,—of oxalic acid, the characteristic constituent of so many plants, and of formic acid, originally discovered in the organism of the ant. With the aid

of the same cyanogen, we prepare artificially urea, the well known alkaloid, continually excreted by the animal economy. Again, acetic acid, the common product of the dry distillation of wood, descending also from organic life through starch, sugar and alcohol, has lately been formed by combining its very elements. We cannot, indeed, obtain acetic acid by bringing these elements, carbon, hydrogen, and oxygen, directly together; this triumph of constructive Chemistry can only be reached through a series of circuitous processes. But this matters not: starch, likewise, before it is converted into vinegar, has to pass through the state of sugar and of alcohol. The great point is, that we are able to perform the task; and this has been of late effected, although the combined efforts of Faraday, Dumas, Kolbe, and Melsens, were required to accomplish it. A current of sulphur-vapour is passed over ignited carbon, when combination takes place, the result being sulphide of carbon, a beautiful and extremely volatile liquid, whose many and daily increasing applications have gained for it general attention. When exposed to the action of chlorine, this sulphide is decomposed, and after a series of processes, we obtain the chloride of carbon, originally discovered by Faraday. This chloride, under the influence of water, is transformed into an acid, known as chloracetic acid, and differing from common vinegar only by containing chlorine, instead of a portion of its hydrogen. A simple substitution of the latter for the former element, completes the series of chemical reactions resulting in the artificial construction of acetic acid. This substitution is effected by potassium, which seizing, as it were, the chlorine, and simultaneously decomposing water, removes the former, whose position is forthwith taken by the liberated hydrogen, thus forming pure acetic acid; and here, remarkably enough, we meet, after nearly half a century, with new consequences of Davy's grand discovery of the decomposition of the alkalies.

These details of the process sufficiently show that it will not serve the purpose of the manufacturer of acetic acid. But this was not required: our methods for obtaining this acid being already simple and cheap. The important point gained by these ingenious experiments is the demonstration of a principle, which is sure to find valuable applications in a multitude of other cases.

All products of organic life are formed from a comparatively small number of inorganic compounds. Carbonic acid, water, ammonia, sulphuric and phosphoric acids are the materials from which vitality builds up the endless variety of substances constituting the organic kingdom. Facts like those, which I have just instanced, encourage us to believe that ultimately we shall find chemical artifices by which we may arrange these same materials into the various compounds elaborated by the processes of vitality. It is for this end that the study of the metamorphoses of organic compounds is of so much value; it is not the host of new substances, which we are continually discovering, that interest us so much, but new methods of operation, by which we may imitate, for our special purposes, the formative forces of nature. Every new reaction with which we become acquainted, is a step nearer to the solution of this grand problem. Take, for instance, one great desideratum, the artificial formation of the natural alkaloids, which are so extensively employed in medicine. Everybody must admit that the discovery of a simple process for preparing artificially the febrifuge principle of the Cinchona-bark, would confer a real blessing upon humanity. Now we have good grounds for the expectation that constructive Chemistry will not long remain without accomplishing this task. Already—and some of the papers contained in the present volume, give ample proof of this assertion—numerous substances have been artificially formed, which are in the closest relation

to quinine and cinchonine. It is a remarkable fact that naphthaline, the beautiful hydrocarbon, of which immense quantities are annually produced in the manufacture of coal-gas, when subjected to a series of chemical processes, may be converted into a crystalline alkaloid. This substance, which has received the name of *napthalidine*, contains: 20 equivalents of carbon, 9 equivalents of hydrogen, and 1 equivalent of nitrogen. The composition of quinine is not finally ascertained, some chemists believe that it contains 19 equivs., others 20 equivs. of carbon. There is a similar difference of opinion with regard to the hydrogen, which by some is stated at 11 equivs., by others at 12 equivs.; the presence of 1 equiv. of nitrogen, and 2 equivs. of oxygen, being generally admitted.

Now, if we take 20 equivs. of carbon, 11 equivs. of hydrogen, 1 equiv. of nitrogen, and 2 equivs. of oxygen, as the composition of quinine, it will be obvious that naphthalidine, differing only by the elements of two equivalents of water, might pass into the former alkaloid simply by an assumption of water. We cannot, of course, expect to induce the water to enter merely by placing it in contact; but a happy experimenter may attain this end by the discovery of an appropriate metamorphic process.

And naphthaline is not the only hydrocarbon which, when subjected to certain chemical processes, may be transformed into an alkaloid. This convertibility has been found a general property of hydrocarbons. Now if we recollect the vast number of these substances actually known, and the manifold sources of similar compounds—such as all sorts of organic matter, when decomposed by heat, &c.—there can remain little doubt that ere long we shall arrive at the alkaloids of the Cinchona-bark, as the result of the prosecution of this inquiry.

This leads us appropriately to notice, in conclusion, the interesting researches of Mr. Mansfield on Coal-Tar, which in this country is our principal source of hydrocarbons. The title of Mr. Mansfield's paper, which concludes the volume, may not seem very inviting to the uninitiated eye. But the unravelling of that complication of oily substances had, in the hands of several chemists, presented us with compounds of the highest interest. Nor is this last contribution devoid of claims on scientific attention, having pointed out inexhaustible sources of several series of compounds, which have long been favourites with the cultivators of organic chemistry; and although it has not yet solved the great problem of constructive chemistry, to which I have above alluded, it has given promises of great practical utility in the arts of life. The coal-naphtha of commerce is a mixture of hydrocarbons of a resultant volatility, and consequent inflammability; too great to admit of its being used in lamps, in which its congener camphine is burned, while its volatility is not sufficient to make it applicable in other cases, in which this property is principally required. Now Mr. Mansfield has succeeded in separating from coal-naphtha a number of different oils, one of which is scarcely to be distinguished in its physical properties from oil of turpentine, while another of them, benzole, is so readily evaporable, as to form a convenient substitute for ether in various instances. In benzole, he has, moreover, found a gas-light, which he considers to be cheaper, and which is more elegant than that of coal-gas, while it is applicable under conditions in which the latter is inadmissible. This is accomplished by passing a stream of common gas of low, or no luminiferous power, or even of atmospheric air, through a reservoir of benzole, wherein it becomes so highly charged with hydrocarbon-vapour, as to burn with a brilliant light, even after circulating through ramified

pipes, like ordinary coal-gas. This process has not yet been tried on a very large scale, but as far as we can judge from the results obtained with a small apparatus, the proposition of Mr. Mansfield appears to be very promising. The same gentleman has also found that by mixing pyroxylic spirit with some of the hydrocarbons of coal-tar, a liquid fuel is produced, which supplies self-generating gas to ordinary table-lamps. Nor is the sense of sight the only one which benzole promises to serve. By treatment with nitric acid, the same volatile hydrocarbon yields a fragrant oil, the odour of which is not to be distinguished from that of oil of bitter almonds; so that this perfume may now be procured from coal-tar in tons, if required, with the greatest facility, and at a trifling cost. Other applications of this remarkable hydrocarbon will be found in the paper alluded to.

A. W. H.

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# RESEARCHES

IN

# INORGANIC CHEMISTRY.

## I.—*Analysis of the Water of the Thermal Spring of Bath (King's Bath).*

By George Merck and Robert Galloway, Esqrs.

(Read before the Chemical Society of London, December, 1846.)

The water of this celebrated spring, the efficacy of which was known in the time of the Romans, has been analysed repeatedly by various chemists at different periods. Richard Phillips,* Scudamore,† Walker,‡ and more recently Noad,§ have occupied themselves in the investigation of this water. In their several analyses, the whole amount of the fixed ingredients of the water agrees very closely; but in regard to the composition of these substances there are considerable discrepancies, as may be seen in a table which we have annexed at the end of this paper.

Besides great differences in the quantitative analysis, we find discrepancies even in regard to the presence and absence of certain constituents. Among the chemists that have been mentioned, Walker is the only one who has recognised the presence of potassa. The same chemist corroborated Scudamore's statement as to the presence of magnesia, overlooked by their predecessors; but he states also that he detected alumina, which none of the others found. In all these analyses iodine has been omitted. Mr. Cuff,‖ however, has indicated the presence of this element in the spring.

* An Analysis of the Bath Water, by Richard Phillips. London, 1806.

† A Chemical and Medical Report of the properties of the Mineral Waters of Buxton, Matlock, &c., by Ch. Scudamore, M.D., 1820.

‡ Quarterly Journal of Science, Literature and Arts, vol. xxvii. p. 78, 1829.

§ Pharmaceutical Journal, vol. iii. 526.

‖ Memoir on the occurrence of Iodine and Bromine in certain Mineral Waters of South Britain, by Charles Daubeny; Transactions of the Royal Society of London, 1830, vol. ii. p. 223.

These discrepancies made another investigation of the mineral water of Bath very desirable; the following analysis was performed at the suggestion and under the direction of Dr. Hofmann.

To obtain the water genuine, and especially for the purpose of ascertaining the amount of free carbonic acid it contained, we collected the water ourselves, an operation in which we were kindly assisted by Messrs. Green and Simms, lessees of the establishment.

The water was taken from the principal well, which supplies the King's and Queen's baths, which are the most esteemed and valued in the city. Of the two other wells, one supplies the Hot Bath and the other the Cross Bath, which are in the neighbourhood of those first mentioned.

The King's Bath is an oblong cistern, 65 feet long and 40 feet broad, in which the water stands at the height of 46 inches. It is supplied from the bottom by means of twelve large and about twenty smaller apertures. By far the largest amount of water rises however from an opening made in the centre of the bath, 18 inches in diameter. Although the water flows under the influence of a very small pressure, the quantity is such, that the two reservoirs, the King's and the Queen's Bath, are entirely filled in about nine hours. The quantity of water entering each minute is 126 gallons, upon the authority of Dr. Daubeny.*

## I. QUALITATIVE ANALYSIS.

The water as it issues from the well has a temperature of 40° C. (115° Fahr.), the temperature of the air being 20° C. (68° Fahr.); it is clear and without odour, and has no effect upon vegetal colours; it has a saline and slight iron taste; the iron is deposited as sesquioxide in rather large quantities in the pipes leading from the well.

The following experiments gave the qualitative composition of the mineral water; on boiling for some time a white crystalline precipitate formed. The qualitative analysis was therefore divided into two parts.

*a*. The analysis of the precipitate formed on boiling.

*b*. The analysis of the substances remaining dissolved.

### *a*. ANALYSIS OF THE PRECIPITATE FORMED ON BOILING.

1. The precipitate was treated with hydrochloric acid; a small portion of it dissolved with effervescence, indicating the presence

* On the Quantity and Quality of the Gases disengaged from the Thermal Spring which supplies the King's Bath in the City of Bath, by Charles Daubeny; Transactions of the Royal Society of London, 1834, I. i.

of carbonic acid. The portion insoluble in hydrochloric acid dissolved on the addition of a large quantity of water:—*Indicating sulphate of lime.*

Another portion of the water was boiled some time, with the precaution of replacing the evaporated water, in order that all the sulphate of lime should remain in solution; in this case only a very small precipitate was formed, which was entirely soluble in hydrochloric acid.

2. On heating this solution and adding ammonia, a very slight flocculent precipitate of a yellowish-white colour was produced after some time:—*Indicating oxide of iron.*

3. In the filtrate from the sesquioxide of iron (2), on the addition of oxalate of ammonia, a white precipitate was formed:—*Indicating salts of lime.*

4. In the liquid filtered off from the oxalate of lime (3), phosphate of soda produced an exceedingly slight crystalline precipitate:—*Showing the presence of magnesia.*

This precipitate could only be distinctly seen in testing a large quantity of the water.

### *b.* ANALYSIS OF THE SUBSTANCES REMAINING DISSOLVED.

The liquid which was filtered from the precipitate (*a*), formed on boiling, had no alkaline reaction; a portion of it was evaporated nearly to dryness and treated with hydrochloric acid; no carbonic acid was evolved, from which comportment the absence of alkaline carbonates could with safety be concluded.

1. A portion of the liquid gave, on addition of chloride of barium, a copious white precipitate, insoluble in hydrochloric acid:—*Indicating sulphuric acid.*

2. In another portion of the liquid, nitrate of silver produced a copious white precipitate, easily soluble in ammonia:—*Proving the presence of chlorine.*

3. The entire solubility of the silver precipitate seemed to indicate the absence of iodides. To make ourselves perfectly certain of the absence of these salts, 30 or 40 pounds of the water were evaporated to 2 or 3 pounds, and the liquid filtered off from the precipitate which had been formed; a part of this fluid was evaporated with precaution to dryness, the residue was mixed with some starch paste, and a few drops of nitric acid being added, feeble but distinct violet spots were observed: this experiment was repeated several times with the same success:—*Indicating the presence of iodine.*

4. Another portion of the liquid (*b*), was treated with hydrochloric

acid, evaporated to dryness, and gently ignited: on treating the residue with a large quantity of water an insoluble portion remained: —*Showing the presence of silicic acid.*

5. Another portion of the liquid (*b*) gave, on addition of chloride of ammonium and oxalate of ammonia, a white precipitate:—*Indicating lime.*

6. On adding, to a portion of the filtrate, ammonia and phosphate of soda, a slight crystalline precipitate was formed:—*Indicating magnesia.*

7. For the detection of the alkalies, the remaining portion of the filtrate from the lime precipitate was evaporated to dryness, and the residue ignited until the ammoniacal salts had been expelled. The ignited residue was then dissolved in water, the sulphuric acid and magnesia precipitated by baryta water, and after separation of the excess of baryta by means of carbonate of ammonia, the filtrate evaporated to dryness and ignited. The residue imparted a yellow colour to the blow-pipe flame:—*Proving the presence of soda.*

An alcoholic solution of the residue gave with a concentrated solution of bichloride of platinum a yellow crystalline precipitate:—*Indicating potassa.*

The precipitate which had formed on evaporating for the iodine determination, was treated with hydrochloric acid, the filtrate saturated with ammonia and precipitated by sulphide of ammonium; this precipitate was re-dissolved in nitro-hydrochloric acid mixed with chloride of ammonium, and the sesquioxide of iron separated by ammonia. The filtrate, evaporated and fused with nitrate of potassa and carbonate of soda, gave a green mass:—*Showing traces of manganese.*

Lithia, alumina, bromine and phosphoric acid were found to be absent.

With regard to the presence of gases in the water, it was scarcely requisite to convince ourselves further of the presence of free carbonic acid. To prove, however, the presence of this acid beyond a doubt, the following experiment was made: a portion of the mineral water was treated with a solution of lime; a precipitate was formed which dissolved on a further addition of the water. The quantity of free carbonic acid, however, is not very great, the water having no reaction on blue vegetal colours.

The Bath water does not contain hydrosulphuric acid, for on addition of acetate of lead, a perfectly white precipitate of sulphate of lead was obtained, proving the absence of this gas.

A large quantity of gas is continually disengaged from the chief

spring as well as from the secondary ones. Dr. Daubeny* paid particular attention to the composition of this gas. He found that it consists principally of nitrogen, together with small quantities of carbonic acid and oxygen.

He employed a peculiar apparatus, constructed on purpose for these experiments, by which he was enabled to collect the whole of the gases from the principal spring, as well as from those adjoining it. The experiments of Daubeny are so numerous and accurate as to preclude any other researches on the subject.

## II. QUANTITATIVE ANALYSIS.

### DETERMINATION OF THE SPECIFIC GRAVITY.

A small bottle, which contained at the temperature of 15·5° C. (60° Fahr.) 10 grm. of distilled water, contained at the same temperature 10·025 grm. of the mineral water; from this the specific gravity of the water is calculated as 1·0025.

The different quantities of water employed in the quantitative analyses were all accurately weighed in preference to measuring them.

### 1. ESTIMATION OF SULPHURIC ACID.

The mineral water was heated with a little hydrochloric acid and chloride of barium added.

I. 534·199 grm. of water gave 1·340 grm. of sulphate of baryta = 0·4605 grm., or 0·08620 per cent. of sulphuric acid.

II. 475.003 grm. of water gave 1·1791 grm. of sulphate of baryta = 0·4050 grm., or 0·08526 per cent. of sulphuric acid.

Mean of the results, 0·08573 per cent.

### 2. ESTIMATION OF CHLORINE.

The water was treated with nitric acid and precipitated by nitrate of silver; the precipitated chloride of silver was washed by decantation, fused and weighed.

I. 101 grm. of water gave 0·1137 grm. of chloride of silver = 0·2811 grm. or 0·02778 per cent. of chlorine.

II. 100·006 grm. of water gave 0·1093 grm. of chloride of silver = 0·02702 grm. or 0·02701 per cent. of chlorine.

Mean of the results, 0·02739 per cent.

### 3. ESTIMATION OF SILICIC ACID.

To the water was added nitric acid in excess; it was then evaporated to dryness and the residue for some time heated on the sand-

* Vide Memoir mentioned.

bath. On treating this residue with water and hydrochloric acid, the silicic acid remained behind; it was collected, washed and weighed.

I. 765·325 grm. of the water gave 0·0342 grm. or 0·00446 per cent. of silicic acid.

II. 732·015 grm. of water gave 0·0289 grm. or 0·00407 per cent. of silicic acid.

Mean of the results, 0·00426 per cent.

### 4. ESTIMATION OF SESQUIOXIDE OF IRON.

To estimate the total amount of iron, lime, and magnesia, the liquid filtered off from the silicic acid was concentrated, and the iron then precipitated by excess of ammonia.

I. 765·325 grm. of water gave 0·0078 grm. or 0·00101 per cent. of sesquioxide of iron.

II. 732·015 grm. of water gave 0·0086 grm. or 0·00116 per cent. of sesquioxide of iron.

Mean of the results, 0·00108 per cent.

### 5. ESTIMATION OF LIME.

The lime was precipitated from the ammoniacal filtrate, after addition of chloride of ammonium, by oxalate of ammonia, and the oxalate of lime converted in the known way into carbonate.

I. 765·325 grm. of water gave 0·7211 grm. of carbonate of lime = 0·403816 grm. or 0·05276 per cent. of lime.

II. 732·015 grm. of water gave 0·6981 grm. of carbonate of lime = 0·3909 grm. or 0·05340 per cent. of lime.

Mean of the results 0·05308 per cent.

### 6. ESTIMATION OF MAGNESIA.

The magnesia was precipitated in the filtrate from the oxalate of lime precipitate, by addition of ammonia and phosphate of soda.

I. 765·325 grm. of water gave 0·1936 grm. of pyrophosphate of magnesia = 0·070929 grm. or 0·00926 per cent. of magnesia.

II. 732·015 grm. of water gave 0·1837 grm. of pyrophosphate of magnesia = 0·0673 grm. or 0·00919 per cent. of magnesia.

Mean of the results 0·00922 per cent.

The above estimations of iron, lime, and magnesia, were controlled by the following determinations of those substances in their different states.

To estimate the amount of iron, lime, and magnesia in the state of carbonates, a known quantity of the water was boiled in a glass

flask for some hours, adding from time to time distilled water to compensate for the loss by evaporation. The precipitate thus formed was washed, until the washings no longer gave a precipitate with chloride of barium. (The filtrate from this precipitate was reserved for further operations). The precipitate was dissolved in hydrochloric acid, evaporated to dryness, and redissolved in dilute acid; excess of ammonia was then added to precipitate the iron. 777·215 grm. of water gave 0·0079 grm. or 0·00101 per cent. of sesquioxide of iron.

The ammoniacal liquor filtered from the precipitate of sesquioxide of iron, was precipitated by oxalate of ammonia; the oxalate of lime was converted into carbonate.

I. 712·747 grm. of water gave, on boiling, a precipitate, containing 0·0904 grm. of carbonate of lime = 0·05062 grm. or 0·00712 per cent. of lime.

II. 623·881 grm. of water gave, on boiling, a precipitate, containing 0·0782 grm. of carbonate of lime = 0·0437 grm. or 0·00700 per cent. of lime.

Mean of the results, 0·00706 per cent.

To the liquid filtered off from the oxalate of lime, was added phosphate of soda; on stirring, a precipitate of phosphate of magnesia and ammonia was formed, which was converted by ignition into pyrophosphate of magnesia.

I. 777·215 grm. of water gave, on boiling, a precipitate which contained 0·0046 grm. of pyrophosphate of magnesia = 0·001685 grm. or 0·00021 per cent. of magnesia.

II. 623·881 grm. of water gave, on boiling, a precipitate which contained 0·0044 grm. of pyrophosphate of magnesia = 0·00016 grm. or 0·00025 per cent of magnesia.

Mean of the results, 0·00023 per cent.

To estimate the amount of lime which existed as sulphate, and the magnesium which existed as chloride, the filtrate from the precipitate formed on boiling, was evaporated to dryness with a little free hydrochloric acid. It was re-dissolved in water; chloride of ammonium, ammonia, and oxalate of ammonia were then added, and the oxalate of lime was converted into carbonate.

I. 710·747 grm. of water gave, in this way, 0·6072 grm. of carbonate of lime = 0·3400 grm. or 0·04783 per cent. of lime.

II. 623·881 grm. of water gave 0·5165 grm. of carbonate of lime = 0·2892 grm. or 0·04635 per cent of lime.

Mean of results, 0·04709 per cent.

| | |
|---|---|
| Mean of lime combined with carbonic acid . . | 0·00706 |
| Mean of lime combined with sulphuric acid . . | 0·04709 |
| Total amount found by addition . . . . . | 0·05415 |
| Mean of the total amount found by direct estimation . . . . . | 0·05308 |

The magnesia was precipitated in the filtrate from the oxalate of lime by phosphate of soda.

I. 414·279 grm. of water gave, in this way, 0·1007 grm. of pyrophosphate of magnesia = 0·03689 grm. or 0·008906 per cent. of magnesia.

II. 427·1 grm. of water gave 0·1050 grm. of pyrophosphate of magnesia = 0·03846 grm. or 0·009004 per cent. of magnesia.

Mean of the results, 0·008955 per cent.

| | |
|---|---|
| Mean of the magnesia combined with carbonic acid | 0·00023 |
| Mean of the magnesia contained in the water as chloride of magnesium . . . . . | 0·00895 |
| Total amount found by addition . . . . . | 0·00918 |
| Mean of the total amount found by direct estimation . . . . . | 0·00922 |

### 7. ESTIMATION OF THE ALKALIES.

For the estimation of the alkalies, the mineral water was evaporated to one third of its volume, and baryta water added in excess; the precipitate of sulphates of baryta, lime, magnesia, and of sesquioxide of iron was filtered off, and the excess of baryta precipitated by means of carbonate of ammonia. To get rid of the silicic acid, the filtrate was evaporated to dryness with hydrochloric acid, gently ignited, dissolved in water, again filtered and evaporated to dryness; the mixed chlorides obtained in this manner were weighed.

I. 632·481 grm. of the mineral water gave 0·2937 grm. of chloride of sodium and chloride of potassium = 0·04643 per cent. of the mixed chlorides.

II. 546·032 grm. of water gave 0·2538 grm. of chlorides of sodium and potassium = 0·04648 per cent. of the mixed chlorides.

Mean of the results, 0·04645 per cent.

### 8. ESTIMATION OF POTASSA.

The chlorides of potassium and sodium were dissolved in a small quantity of water and an excess of bichloride of platinum added; the liquid was then evaporated to dryness in the water-bath, the residue digested with alcohol, the insoluble bichloride of platinum and potassium filtered off from the soluble sodium salt and washed with alcohol; the precipitate was dried in the water-bath and weighed.

I. 632·481 grm. of the mineral water, or 0·2987 grm. of the mixed chlorides, gave 0·124 grm. of bichloride of platinum and potassium = 0·0378 grm. of chloride of potassium = 0·00597 per cent. of chloride of potassium, which equals 0·00377 per cent. of potassa.

II. 546·032 grm. of water, or 0·2538 grm. of the mixed chlorides, gave 0·0975 grm. of bichloride of platinum and potassium = 0·02977 grm. of chloride of potassium = 0·00545 per cent. of chloride of potassium, which equals 0·00342 per cent. of potassa.

Mean of the results, 0·00571 per cent. of chloride of potassium and 0·0359 per cent. of potassa.

### 9. ESTIMATION OF SODA.

The quantity of soda was found simply by the difference of the mixed chlorides and the quantity of chloride of potassium found by direct estimation.

| | |
|---|---|
| Mean of the mixed chlorides . . . | 0·04645 |
| Mean of the chloride of potassium . | 0·00571 |
| Chloride of sodium . . | 0·04074 |

corresponding to 0·02168 per cent. of soda.

### 10. ESTIMATION OF CARBONIC ACID.

To find the quantity of free carbonic acid contained in the water at the moment it was taken from the well, a syphon of exactly known capacity was immersed in the well, and the water obtained in this way put in bottles, containing a mixture of ammonia and chloride of calcium. In this way the free carbonic acid as well as the carbonic acid in combination was precipitated in the form of carbonates. Four bottles were filled with mineral water by this method. The capacity of the syphon was exactly 533 cubic centimetres, therefore $533 \times 4 \times 1{\cdot}0025 = 2137$ grm. of water were taken.

The precipitate from the water contained in these four bottles was collected, washed, dried, and weighed; it yielded 1·4748 grm. of

carbonate mixed with some alumina from the solution of chloride of calcium.

To estimate the quantity of carbonic acid in this precipitate, two portions of it were taken and estimated separately after the method proposed by Drs. Fresenius and Will.

I. 0·66 grm. of the carbonate, &c. gave in this way 0·22 grm. of carbonic acid, therefore 1·4748 grm. of the carbonate, or 2137·0 grm. of water, gave 0·4916 grm. of carbonic acid.

II. 0·718 grm. of the carbonate, &c. gave 0·23 grm. of carbonic acid, therefore 1·4748 grm. of the carbonate, &c., or 2137·0 grm. of water, gave 0·4718 grm. of carbonic acid.

MEAN OF THE RESULTS.

| | | | |
|---|---|---|---|
| 0·4817 grm. of carbonic acid, which equals | | 0·02254 | per cent. |
| Total amount of carbonic acid . . . | | 0·02254 | „ „ |
| Carbonic acid existing in combination— | | | |
| With protoxide of iron . . | 0·00057 | | |
| With lime . . . . . | 0·00554 | | |
| With magnesia . . . . | 0·00024 | | |
| Sum total . . . . . | | 0.00635 | „ „ |
| Free carbonic acid remaining | | 0·01619 | „ „ |

From the details contained in the preceding pages, it follows that the thermal spring in the King's Bath contains the following constituents in 100 parts:

| | |
|---|---|
| Carbonate of lime . . . | 0·01260 |
| Carbonate of magnesia . . | 0·00047 |
| Carbonate of protoxide of iron | 0·00153 |
| Sulphate of lime . . . . | 0·11436 |
| Sulphate of potassa . . . | 0·00663 |
| Sulphate of soda . . . . | 0·02747 |
| Chloride of sodium . . . | 0·01806 |
| Chloride of magnesium . . | 0·02083 |
| Silicic acid . . . . . | 0·00426 |
| Manganese . . . . . | a trace |
| Iodine . . . . . | a trace |
| | 0·20621 |

ESTIMATION OF THE TOTAL AMOUNT OF THE FIXED INGREDIENTS IN THE WATER FOR CONTROL.

The water was concentrated in a porcelain dish, and afterwards

evaporated to dryness in a platinum basin. The residue was heated in an air-bath until the weight was constant. Two estimations were made.

I. 217·058 grm. of water gave 0·4540 grm., or 0·20916 per cent. of residue.

II. 319·57 grm. of water gave 0·6726 grm., or 0·21040 per cent. of residue.

Mean of the results, 0·20978 per cent.

But in this experiment the iron was obtained in the state of sesquioxide, whilst in the preceding calculation it is taken as the carbonate of the oxide, in which form it exists in the water.

On calculating the absolute weights from the above, we obtain the following numbers:—

| | In 100 litres. | In an imperial gallon (70,000 grs.) |
|---|---|---|
| Carbonate of lime . . . | 12·6000 grm. | 8·82000 grs. |
| Carbonate of magnesia . . | 0·4700 „ | 0·32900 „ |
| Carbonate of protoxide of iron . | 1·5300 „ | 1·07100 „ |
| Sulphate of lime . . . | 114·3600 „ | 80·05200 „ |
| Sulphate of potassa . . . | 6·6300 „ | 4·64100 „ |
| Sulphate of soda . . . | 27·4700 „ | 19·22900 „ |
| Chloride of sodium . . . | 18·0600 „ | 12·64200 „ |
| Chloride of magnesium . . | 20·8300 „ | 14·58100 „ |
| Silicic acid . . . . . | 4·2600 „ | 2·98200 „ |
| | 206·2100 „ | 144·01800 „ |

According to our experiments, 1 litre of the water contains 95·64 cubic centimetres of free carbonic acid at the temperature of 46° C. (115° F.) and normal atmospheric pressure.

One imperial gallon contains therefore 26·45 cubic inches of carbonic acid at 46° C., being more than double the quantity which has been determined by former experiments.

This, however, is not surprising, as the estimations previously made had been effected by the expulsion of the carbonic acid from the water. Besides the difficulty of avoiding a loss of carbonic acid before the operation, it is scarcely possible, as Mr. Phillips justly notices in his paper, to expel all carbonic acid by simple ebullition. Besides, we see from the experiments of Daubeny, that the gas which escapes from the well contains at different periods highly varying amounts of carbonic acid. He found, by several experiments, that the King's Bath evolves on an average 267 cubic inches of gas

per minute, or 223 cubic feet in twenty-four hours. He further ascertained that this gas consists nearly entirely of nitrogen, mixed with a small amount of oxygen and carbonic acid, and that these gases were generally in the following proportion:—

| | |
|---|---|
| Nitrogen . . . | = 91·9 |
| Oxygen . . . . | = 3·8 |
| Carbonic acid . . | = 4·3 |

In many instances, however, he observed as much as 7·4 to 8·2, and even once 11·5 parts of carbonic acid.

From these observations there is no doubt that the quantity of carbonic acid dissolved in the water is very variable.

In the following Table we give the analyses of former experimenters, calculated in an imperial gallon (70·000 grs.)

| | Phillips. | Scudamore.* | Walker. | Noad. |
|---|---|---|---|---|
| Carbonate of lime . . . | 7·680 | 5·280 | 10·667 | |
| Carbon. of protoxide of iron | 0·274 | 0·200 | 0·243 | 0·521 |
| Carbonate of soda . . . | — | — | — | 5·760 |
| Sulphate of lime . . . . | 86·400 | 98·320 | 81·624 | 96·240 |
| Sulphate of potassa . . . | — | — | 2·927 | |
| Sulphate of soda . . . . | 14·400 | 1·520 | 19·371 | |
| Chloride of sodium . . . | 31·680 | 12·240 | 15·122 | 27·456 |
| Chloride of magnesium . . | — | 15·360 | 13·339 | 7·142 |
| Alumina . . . . . | — | — | 0·150 | |
| Silicic acid . . . . . | 1·960 | 1·920 | 3·233 | 3·360 |
| | 142·394 | 134·840 | 146·676 | 140·479 |
| Quantity directly observed . | 144·125 | — | 147·622 | 149·72 |
| Carbonic acid . . . . . | 11·52 cub. in. | — | 7·60 cub. in. | |

Our analysis agrees, as may be seen, best with that of Walker. According to Professor Liebig's arrangement† of mineral waters, the thermal spring of Bath would belong to the saline waters containing carbonic acid.

* Re-calculated according to a more correct principle by Walker.

† Handwörterbuch der Chemie, Art. 'Analyse der Mineralwasser.'

## II.—*On the Mineral Waters of Cheltenham.*

By F. A. Abel and Thos. H. Rowney, Esqrs.,
assistants at the royal college of chemistry.

(Read before the Chemical Society of London, May 1, 1848.)

The unquestionably beneficial effects of mineral waters in various diseases on the human system, have attracted the attention of chemists from an early period to the composition of medicinal springs.

A great number of analyses of such waters have already been made, but our knowledge scarcely extends beyond that of the general effect produced by them; our speculations regarding the part taken by the individual constituents in the effects produced by mineral waters are very vague and divided. The unsatisfactory state of knowledge on this subject may be ascribed partly to the imperfect nature of most of the analyses, many of which were performed at a period when analytical chemistry was not so far developed as it now is; partly, likewise, to a want of principle and accordance in the arrangement of the results of many of these analytical investigations.

As long as these results are not arranged according to some one principle and rule, it is impossible for the medical man to institute a correct comparison between different waters, and much of the interest and use of such analyses is lost, as it is this comparison of different waters that is most likely to lead to a knowledge of the manner in which the individual constituents act.

An uniform and comparable arrangement of results, is of such primary importance, that the choice of the principle to be adopted is of less moment.

In the following analyses of different mineral waters from Cheltenham, suggested by Dr. Hofmann, the bases and acids have been arranged as much as possible according to their affinities, the strongest bases being supposed in combination with the strongest acids. Such an arrangement may be considered to furnish the nearest approach to the real distribution of the various constituents in the water.

With reference to the classification, this investigation may be regarded as the continuation of a work commenced by Messrs. Merck and Galloway on the analysis of the Bath waters, which is being carried out in the laboratory of the Royal College of Chemistry; where the analysis of a series of mineral waters, according to the system above described, is contemplated.

In order to collect the water for analysis ourselves, we visited Cheltenham about the middle of August, 1847.

The springs of Cheltenham—of which there are at present fourteen in use—are distributed over the whole town and surrounding country. They are, however, conducted, by the various proprietors, through iron pipes to four different pump-rooms, which have been erected as near as possible to the principal wells. Having ascertained that many of the waters were very similar in properties and constitution, and as it would consequently have been an useless repetition to analyse the whole of them, we determined to select from among them, those that would best illustrate the entire series. As the waters of Montpelier Spa have been very recently analysed by Mr. J. T. Cooper, we selected such from the other spas as had never been investigated, or the analysis of which were of rather an ancient date. The waters chosen by us were the Cambray chalybeate spring, the two principal waters of the Royal Old Wells, and the so-called strong saline water of the Pitville Spa. We fixed upon the latter especially, on account of the discrepancies in the published analyses by Daniel, Daubeny, and Buckmann.

The operations at the wells were the same as those generally performed; the only difficulty encountered, consisted in collecting the water for the determination of the gases contained therein. The wells being of great depth, and narrow in bore, it was impossible to descend, in order to dip the water by means of the usual syphon, nor could we lower a vessel, on account of the large cross-beams which traverse the insides of the wells; we were, therefore, compelled to content ourselves with filling the syphon from the force-pumps, and as these were worked but slowly, drawing the water from the bottom of the well, we did not anticipate any very considerable loss of gases. In our paper on the "Artesian Wells of Trafalgar Square," we have shown by experiment, that the loss of carbonic acid, in the process of pumping up the water, is very trifling.

### I. CAMBRAY CHALYBEATE WATER.

This well was discovered in 1807, at Cambray, on the north side of the Chelt. (In 1803, a chalybeate water was discovered on the south side, which was subsequently closed up). It is situated under the kitchen floor of the proprietor's house; the water is conducted from thence, by means of iron pipes, over the little river Chelt to the pump-room, about 100 yards from the spring. The depth of the well is only about 7 feet. The temperature of the water at the time

of observation was 18° C. (64·4° F.) the temperature of the air being 25° C. (77° F.) This water is liable to vary exceedingly in temperature, the well itself being under a house, and the pipe through which the water is conducted being near the surface, and in some places quite exposed. The reaction of the water is alkaline, it has a slight odour of hydrosulphuric acid, besides a very peculiar smell, similar to that of decomposing vegetable matter. Its taste is like that of all waters of this description. Its specific gravity we found to be 1·0010 at 16·5° C. (62·7° F.) The water is perfectly clear when it issues from the pump, but becomes turbid almost immediately on standing, even in close vessels, depositing a quantity of sesquioxide of iron, with which all the vessels used in collecting the water are incrusted. By qualitative analysis, the water was found to contain a minute quantity of sulphuric acid, besides chlorine, carbonic, phosphoric and silicic acids, iron, lime, magnesia, potassa, soda and organic matter. No bromine or iodine could be detected. A portion of the soda was found to exist as carbonate.

By quantitative analysis the following numbers were obtained :

*A.* Determination of the amount of fixed residue.

| Water employed. | Amount of residue obtained. | Per centage in the water. |
|---|---|---|
| 735·545 grm. | 0·4759 grm. | 0·0647 |

*B.* Determination of chlorine.

| Water employed. | Silver-salt obtained. | Per centage of chlorine in the water. |
|---|---|---|
| I. 203·080 grm. | 0·0364 grm. | 0·00444 |
| II. 232·942 „ | 0·0428 „ | 0·00454 |
| | | *Mean* 0·00449 |

*C.* Determination of silicic acid.

| Water employed. | Silicic acid obtained. | Per centage in the water. |
|---|---|---|
| I. 616·402 grm. | 0·0055 grm. | 0·00090 |
| II. 657·820 „ | 0·0072 „ | 0·00109 |
| | | *Mean* 0·00954 |

*D.* Determination of lime.

| Water employed. | Carbonate of lime. | Per centage of lime in the water. |
|---|---|---|
| I. 616·402 grm. | 0·2255 grm. | 0·02049 |
| II. 657·820 „ | 0·2420 „ | 0·02050 |
| | | *Mean* 0·020495 |

*E.* Determination of iron.

| Water employed. | Sesquioxide of iron obtained. | Per centage of protoxide of iron. |
|---|---|---|
| I. 616·402 grm. | 0·0177 grm. | 0·00258 |
| II. 657·820 „ | 0·0168 „ | 0·002553 |
| | | *Mean* 0·0025665 |

*F.* Determination of magnesia.

| Water employed. | Pyrophosphate of magnesia. | Per centage of magnesia. |
|---|---|---|
| I. 616·402 grm. | 0·0534 grm. | 0·00316 |
| II. 657·820 „ | 0·0517 „ | 0·002879 |
| | | *Mean* 0·0030195 |

*G.* Determination of the alkalies.

*a.* Estimation of the mixed chlorides.

| Water employed. | Mixed chlorides obtained. | Per centage in the water. |
|---|---|---|
| I. 619·291 grm. | 0·0999 grm. | 0·01613 |
| II. 578·692 „ | 0·0935 „ | 0·01615 |

*b.* Estimation of potassa.

| Water employed. | Chloride of potassium and platinum. | Per centage of potassa. |
|---|---|---|
| I. 619·291 grm. | 0·1550 grm. | 0·00481 |
| II. 578·692 „ | 0·1515 „ | 0·00502 |
| | | *Mean* 0·00492 |

For the determination of the small quantities of sulphuric and phosphoric acids, and the organic matter existing as apocrenic and crenic acids, and extractive matter, 40·04 lbs., or 18160·3422 grm. were evaporated to 405 grm. The precipitate obtained amounted to 9·4986 grm. and the filtrate, together with the washings, to 589·745 grm.

The sulphuric acid and extractive matter were determined in the filtrate (*a*), the phosphoric, crenic and apocrenic acids in the precipitate (*b*).

*H.* Determination of sulphuric acid.

| Amount of filtrate (*a*) employed. | Sulphate of baryta obtained. | Per centage of sulphuric acid in the water. |
|---|---|---|
| I. 10·772 grm. | 0·3047 grm. | 0·000315 |
| II. 96·800 „ | 0·2702 „ | 0·000313 |
| | | *Mean* 0·000341 |

*I.* Determination of phosphoric acid.

| Amount of precipitate (*b*). | Pyrophosphate of magnesia obtained. | Per centage of phosphoric acid in the water. |
|---|---|---|
| 1·4430 grm. | 0·0167 grm. | 0·000383 |

*K.* Determination of apocrenic acid.

| Amount of precipitate (*b*). | Copper-salt obtained. | Per centage of apocrenic acid in the water. |
|---|---|---|
| 1·4251 grm. | 0·0100 grm. | 0·00021 |

*L.* Determination of crenic acid.

| Amount of precipitate (*b*). | Copper-salt obtained. | Per centage of crenic acid in the water. |
|---|---|---|
| 1·4251 grm. | 0·0359 grm. | 0·0003467 |

*M.* Determination of carbonic acid.

533·533 cubic centimetres of the water yielded on treatment with chloride of calcium and ammonia in the usual manner, 1·6201 grm. precipitate, in which the carbonic acid was determined.

| Amount of precipitate. | Carbonic acid. | Per centage in the precipitate. | Per centage in the water. |
|---|---|---|---|
| I. 0·5095 grm. | 0·1750 | 34·3493 | 0·03466 |
| II. 0·4717 „ | 0·1610 | 34·1320 | |

## II.—PITVILLE SALINE WATER.

This water is procured from five wells, situated under the building or in the vicinity of the Spa. These wells empty themselves, by pipes, into the main well, 90 feet in depth, which is situated under the pump-room. The temperature of the water was, at the time of observation, 14° C. (57·2° F.), that of the air being 19·5° C. (67° F.) Its reaction is strongly alkaline, it has a very slight odour of hydrosulphuric acid, and is possessed of a strong, but agreeably saline taste. Its specific gravity is 1·00763 at 15·5° C. (60° F.) It was found to contain a large amount of sulphuric acid, an estimable quantity of bromine, and a distinct trace of iodine. The remaining constituents were the same as those found in the Cambray water, with the exception of iron, of which no trace could be detected. The phosphoric acid was not estimable.

*A.* Determination of fixed residue in the water.

| Water employed. | Amount of residue obtained. | Per centage of residue. |
|---|---|---|
| 153·335 grm. | 1·4142 grm. | 0·922294 |

*B.* Determination of sulphuric acid.

| Water employed. | Sulphate of baryta obtained. | Per centage of sulphuric acid in the water. |
|---|---|---|
| I. 208·09 grm. | 0·5624 grm. | 0·09286 |
| II. 273·206 „ | 0·7377 „ | 0·09277 |
| | | *Mean* 0·092815 |

*C.* Determination of chlorine and bromine.

*a.* Estimation of the precipitate by nitrate of silver.

| Water employed. | Amount of silver-salt. | Per centage of silver-salt. |
|---|---|---|
| I. 57·17 grm. | 0·970 grm. | 1·6966 |
| II. 107·510 „ | 1·8235 „ | 1·6961 |
| | | *Mean* 1·69635 |

*b.* Estimation of the bromine.

A known quantity of the mixed bromide and chloride of silver, perfectly dry, was submitted at a gentle heat, to a stream of dry and pure chlorine gas, the amount of loss gave, by calculation, the amount of bromide of silver in the mixture.

| Silver-salt employed. | Amount of loss. | Per centage of bromide of silver in the mixture. | Per centage of bromine in the water. |
|---|---|---|---|
| I. 1·1108 grm. | 0·0013 grm. | 0·008642 | 0·0036305 |
| II. 0·7667 „ | 0·0009 „ | 0·008673 | 0·0036435 |
| | | | *Mean* 0·0036370 |

*c.* Indirect estimation of chlorine.

| Per centage of mixed silver-salt. | Per centage of chloride in the silver-salt. | Per centage of chlorine in the water. |
|---|---|---|
| 1·69635 | 1·687708 | 0·417370 |
| | 1·687677 | 0·417362 |
| | | *Mean* 0·417366 |

*D.* Determination of silicic acid.

| Water employed. | Amount of silicic acid. | Per centage in the water. |
|---|---|---|
| I. 388·61 grm. | 0·0153 grm. | 0·00394 |
| II. 493·590 „ | 0·0197 „ | 0·00399 |
| | | *Mean* 0·003965 |

*E.* Determination of lime.

| Water employed. | Amount of carbonate of lime. | Per centage of lime in the water. |
|---|---|---|
| I. 388·61 grm. | 0·0427 grm. | 0·006153 |
| II. 493·590 „ | 0·0544 „ | 0·006172 |
| | | *Mean* 0·06162 |

*F.* Determination of magnesia.

| Water employed. | Pyrophosphate of magnesia obtained. | Per centage of magnesia in the water. |
|---|---|---|
| I. 388·61 grm. | 0·0836 grm. | 0·007882 |
| II. 493·590 „ | 0·1062 „ | 0·007883 |
| | | *Mean* 0·0078825 |

*G.* Determination of the alkalies.

*a.* Estimation of the mixed chlorides.

| Water employed. | Amount of mixed chlorides. | Per centage in the water. |
|---|---|---|
| I. 287·53 grm. | 2·468 grm. | 0·85834 |
| II. 204·853 „ | 1·7585 „ | 0·8584 |

*b.* Estimation of potassa.

| Water employed. | Amount of platinum double salt. | Per centage of potassa in the water. |
|---|---|---|
| I. 287·53 grm. | 0·0352 grm. | 0·002356 |
| II. 204·853 „ | 0·0235 „ | 0·00220 |
| | | *Mean* 0·002278 |

54·16 lbs. = 24564·582 grm. of the water were evaporated to 574·58 grm.—8·193 grm. of precipitate (*a*) were obtained; the filtrate (*b*), and washings amounted to 792·1670 grm. There being no apocrenic acid, nor any estimable quantity of phosphoric acid, the substances to be determined in the precipitate and filtrate, were crenic acid and extractive matter.

*H.* Determination of crenic acid.

| Amount of precipitate (*a*) employed. | Copper-salt obtained. | Per centage of crenic acid in the water. |
|---|---|---|
| 0·5515 grm. | 0·0330 grm. | 0·0005137 |

*I.* Determination of extractive matter.

| Amount of filtrate (*b*) employed. | Amount of extractive matter. | Per centage in the water. |
|---|---|---|
| 13·2225 grm. | 0·205 grm. | 0·0049997 |

*K.* Determination of carbonic acid.

1611·20037 cubic centimetres of the water yielded, with chloride of calcium and ammonia, 2·4540 grm. of precipitate, in which the carbonic acid was estimated.

| Precipitate employed. | Amount of carbonic acid. | Per centage of carbonic acid in the precipitate. |
|---|---|---|
| I. 0·660 grm. | 0·230 grm. | 34·85 |
| II. 0·703 „ | 0·245 „ | |
| Per centage of carbonic acid in the water . . | | 0·05306 |

### III. SULPHURETTED SALINE WATER. (NO. 1).

#### ROYAL OLD WELLS.

This, we were told, was the first water in Cheltenham discovered to possess medicinal properties. It was first noticed in 1716, that flocks of pigeons daily resorted to the head of a small stream in a meadow, distant a few furlongs south of the town, for the purpose of feeding on particles of a white salt casually formed from the water by the heat of the sun. The spring, on its first discovery, was found to be about 6 feet below the surface; in 1808 it was sunk and enlarged to the depth of 12 and width of 6 feet; and in 1819 it was further sunk to 72 feet, its present depth. It is situated close to the pump-room. The depth of water in the well, at the time of observation, was found to be 17 feet; the supply is said to be very regular. Its temperature was 14° C. (57·2° F.), that of the air being 22° C. (71·6° F.) It has a slightly alkaline reaction, and a pure saline taste. Although the odour of hydro-sulphuric acid was stronger in this than in the other waters examined by us, the quantity present was not estimable. At 15·5° C. (60° F.) it has the specific gravity 1·0064. By qualitative analysis it was found to contain the same constituents as the Pitville water, besides iron existing as carbonate and phosphate. There are only small traces of potassa and iodine; part of the lime and magnesia exist as soluble salts, which are not precipitated by boiling. The following were the results obtained by quantitative analysis:

*A.* Determination of the fixed residue.

| Water employed. | Amount of residue. | Per centage of residue in the water. |
|---|---|---|
| 199 28 grm. | 1·6291 grm. | 0·817493 |

*B.* Determination of sulphuric acid.

| | Water employed. | Sulphate of baryta obtained. | Per centage of sulphuric acid in the water. |
|---|---|---|---|
| I. | 67·130 grm. | 0·3690 grm. | 0·18887 |
| II. | 69·836 „ | 0·3822 „ | 0·18804 |
| | | | *Mean* 0·188455 |

*C.* Determination of chlorine and bromine.

*a.* Estimation of the mixed chloride and bromide of silver.

| | Water employed. | Silver-salt obtained. | Per centage. |
|---|---|---|---|
| I. | 47·520 grm. | 0·5083 grm. | 1·0696 |
| II. | 58·053 „ | 0·6210 „ | 1·0697 |
| | | | *Mean* 1·06965 |

*b.* Estimation of the bromine.

| | Silver-salt employed. | Amount of loss. | Per centage of bromide of silver. | Per centage of bromine in the water. |
|---|---|---|---|---|
| I. | 0·8554 grm. | 0·0010 grm. | 0·005447 | 0·002288 |
| II. | 1·2619 „ | 0·0015 „ | 0·005538 | 0·002326 |
| | | | | *Mean* 0·002307 |

*c.* Indirect estimation of chlorine.

| Per centage of mixed silver-salt. | Per centage of chloride in the mixture. | Per centage of chlorine in the water. |
|---|---|---|
| 1·06965 | 1·064203 | 0·263155 |
| | 1·064112 | 0·263177 |
| | | *Mean* 0·263166 |

*D.* Determination of silicic acid.

| | Water employed. | Silicic acid obtained. | Per centage in the water. |
|---|---|---|---|
| I. | 421·160 grm. | 0·0060 grm. | 0·001425 |
| II. | 454·320 „ | 0.0067 „ | 0·001470 |
| | | | *Mean* 0·001447 |

*E.* Determination of phosphate of sesquioxide of iron.

| Water employed. | Amount of phosphate of sesquioxide of iron. | Per centage in the water. |
|---|---|---|
| I. 421·160 grm. | 0·0011 grm. | 0·000261 |
| II. 454·320 „ | 0·0012 „ | 0·000264 |
| | | *Mean* 0·002625 |

*F.* Determination of lime.

*a.* Estimation of the total amount of lime.

| Water employed. | Amount of carbonate of lime. | Per centage of lime in the water. |
|---|---|---|
| I. 421·160 grm. | 0·1900 grm. | 0·025263 |
| II. 454·320 „ | 0·2047 „ | 0·025230 |
| | | *Mean* 0·025246 |

A known quantity of water being submitted to brisk ebullition, and the evaporated portion replaced from time to time, a precipitate was formed; the iron, lime and magnesia were determined in the precipitate and filtrate in the usual manner.

*b.* Estimation of lime in the precipitate.

| Water employed. | Amount of carbonate of lime. | Per centage of lime in the water as carbonate. |
|---|---|---|
| I. 432·720 grm. | 0·1365 grm. | 0·01766 |
| II. 433·096 „ | 0·1367 „ | 0·01767 |
| | | *Mean* 0·017665 |

*c.* Estimation of lime in the filtrate.

| Water employed. | Amount of carbonate of lime. | Per centage of lime in the water as soluble salts. |
|---|---|---|
| I. 432·72 grm. | 0·0583 grm. | 0.007544 |
| II. 409·73 „ | 0·0545 „ | 0·007448 |
| | | *Mean* 0·007496 |

*G.* Determination of iron.

*a.* Estimation in the original water.

| Water employed. | Amount of sesquioxide of iron. | Per centage of protoxide of iron. |
|---|---|---|
| I. 421·160 grm. | 0·0025 grm. | 0·000534 |
| II. 454·320 „ | 0·0027 „ | 0·000528 |
| | | *Mean* 0·000531 |

*b*. Estimation in the precipitate formed on boiling.

| Water employed | Amount of sesquioxide of iron. | Per centage of protoxide of iron. |
|---|---|---|
| I. 432·720 grm. | 0·0026 grm. | 0·000540 |
| II. 433·096 „ | 0·0025 „ | 0·000531 |
| | | *Mean* 0·0005355 |

*H*. Determination of magnesia.

*a*. Estimation of the total amount.

| Water employed. | Pyrophosphate of magnesia obtained. | Per centage of magnesia in the water. |
|---|---|---|
| I. 421·160 grm. | 0·3868 grm. | 0·033650 |
| II. 454·320 „ | 0·4192 „ | 0·033807 |
| | | *Mean* 0·033728 |

*b*. Estimation of magnesia in the precipitate formed on boiling.

| Water employed. | Pyrophosphate of magnesia. | Per centage of magnesia in the water as carbonate. |
|---|---|---|
| I. 432·72 grm. | 0·0160 grm. | 0·001354 |
| II. 409·73 „ | 0·0154 „ | 0·001377 |
| | | *Mean* 0·001365 |

*c*. Estimation of magnesia in the filtrate.

| Water employed. | Pyrophosphate of magnesia. | Per centage of magnesia existing as soluble salts. |
|---|---|---|
| I. 432·720 grm. | 0·3800 grm. | 0·032152 |
| II. 433·096 „ | 0·3825 „ | 0·032359 |
| | | *Mean* 0·032455 |

*I*. Determination of soda.

| Water employed. | Chloride of sodium obtained. | Per centage. | Per centage of soda in the water. |
|---|---|---|---|
| I. 21·41 grm. | 0·1290 | 0·6025 | 0·319481 |
| II. 15·01 „ | 0·0896 | 0·5969 | 0·315789 |
| | | | *Mean* 0·317638 |

84·286 lbs. = 38228·40416 grm. of the water were evaporated to 700 grm.—24·5965 grm. of precipitate (*a*), and 3295·7 grm. of filtrate (*b*), were obtained, in which the crenic acid and extractive

matter were determined; apocrenic acid being absent, and phosphoric acid not estimable.

*K.* Determination of crenic acid.

| Precipitate (*a*) employed. | Copper-salt obtained. | Per centage of crenic acid in the water. |
|---|---|---|
| 1·2470 grm. | 0·0180 grm. | 0·024035 |

*L.* Determination of extractive matter.

| Filtrate (*b*) employed. | Amount of extractive matter. | Per centage in the water. |
|---|---|---|
| 50·1 grm. | 0·016 grm. | 0·000033 |

*M.* Determination of carbonic acid.

1609·2336 cubic centimetres of water yielded 2·2525 grm. of precipitate.

| Amount of the precipitate employed. | Amount of carbonic acid. | Per centage in the precipitate. | Per centage in the water. |
|---|---|---|---|
| I. 0·6495 grm. | 0·176 grm. | 27·09 | 0·037883 |
| II. 0·6215 „ | 0·168 „ | 27·03 | |
| | | *Mean* 27·06 | |

## IV. STRONG SALINE WATER. (No. 4.)

### ROYAL OLD WELLS.

This well is situated at a short distance from the former. It is 71 feet deep, the height of the water at the time of examination being 12 feet; the supply at this spring is not so regular as at the former. Besides being conducted to the principal pump-room, the patients may partake of it in a small pump-room close to the well. It was here that the water was collected. Its temperature was 14° C. (57·2° F.), that of the air being 22° C. (71·6° F.) Its reaction is slightly alkaline, its taste saline, and it has a faint odour of hydrosulphuric acid. Its specific gravity is 1·00795 at 15·5° C. (60° F.) Its constituents are similar to those of the former water. The iodine contained in it is estimable; of iron there are only traces, as also of phosphoric acid. The details of the quantitative analysis are as follows:

*A.* Determination of fixed residue in the water.

| Water employed. | Amount of fixed residue, | Per centage in the water. |
|---|---|---|
| 34·935 grm. | 0·3702 grm. | 1·059682 |

*B.* Determination of sulphuric acid.

| Water employed. | Sulphate of baryta obtained. | Per centage of sulphuric acid in the water. |
|---|---|---|
| I. 42·270 grm. | 0·0940 grm. | 0·076408 |
| II. 75·110 „ | 0·1672 „ | 0·076480 |
| | | *Mean* 0·076444 |

*C.* Determination of chlorine and bromine.

*a.* Estimation of the mixed silver-salt.

| Water employed. | Amount of silver-salt. | Per centage in the water. |
|---|---|---|
| I. 27·496 grm. | 0·5820 grm. | 2·1166 |
| II. 55·193 „ | 1·1660 „ | 2·1125 |
| | | *Mean* 2·11455 |

*b.* Estimation of bromine in the silver precipitate.

Some of the mixed silver-salt was exposed, as before, to a stream of dry chlorine. From the amount of loss, the joint amount of bromide and iodide of silver in the precipitate was calculated.

| Silver-salt employed. | Amount of loss. | Per centage of mixed bromide and iodide of silver. |
|---|---|---|
| I. 1·1813 grm. | 0·0018 grm. | 0·010143 |
| II. 1·0761 „ | 0·0016 „ | 0·009895 |
| | | *Mean* 0·010019 |

The per centage of iodide of silver is calculated from that of the iodine, obtained as described below, and deducted from the above per centage of mixed bromide and iodide of silver. The remaining 0·008968 per cent. of bromide of silver corresponds to 0·003767 per cent. of bromine in the water.

*c.* Indirect estimation of chlorine.

The per centage of bromide and iodide of silver being deducted from that of the mixed silver precipitate, leaves 2·104531 per cent of chloride of silver, corresponding to 0·52045 per cent. of chlorine in the water.

*D.* Determination of silicic acid.

| Water employed. | Amount of silicic acid. | Per centage in the water. |
|---|---|---|
| I. 326·105 grm. | 0·0126 grm. | 0·003864 |
| II. 343·853 „ | 0·0137 „ | 0·003984 |
| | | *Mean* 0·003924 |

*E.* Determination of lime.

*a.* Estimation of the total amount.

| Water employed. | Carbonate of lime obtained. | Per centage of lime in the water. |
|---|---|---|
| I. 326·105 grm. | 0·0796 grm. | 0·013669 |
| II. 343·853 „ | 0·0837 „ | 0·013630 |
| | | *Mean* 0·013649 |

*b.* Estimation of lime in the precipitate formed on boiling the water.

| Water employed. | Carbonate of lime obtained. | Per centage of lime existing in the water as carbonate. |
|---|---|---|
| I. 469·950 grm. | 0·0721 grm. | 0·008591 |
| II. 454·536 „ | 0·0697 „ | 0·008587 |
| | | *Mean* 0·008589 |

*c.* Estimation of lime in the filtrate from the precipitate.

| Water employed. | Carbonate of lime obtained. | Per centage of lime existing in the water as soluble salts. |
|---|---|---|
| I. 469·950 grm. | 0·0410 grm. | 0·004886 |
| II. 454·536 „ | 0·0402 „ | 0·004950 |
| | | *Mean* 0·004918 |

*F.* Determination of magnesia.

*a.* Estimation of the total amount of magnesia.

| Water employed. | Pyrophosphate of magnesia obtained. | Per centage of magnesia in the water. |
|---|---|---|
| I. 326·105 grm. | 0·0960 grm. | 0·010786 |
| II. 343·853 „ | 0·1017 „ | 0·010836 |
| | | *Mean* 0·010811 |

*b.* Estimation of magnesia in the precipitate formed on boiling.

| Water employed. | Pyrophosphate of magnesia obtained. | Per centage of magnesia as carbonate. |
|---|---|---|
| I. 469·950 grm. | 0·0266 grm. | 0·002284 |
| II. 454·536 „ | 0·0282 „ | 0.002273 |
| | | *Mean* 0·002278 |

*c.* Estimation of magnesia in the filtrate.

| Water employed. | Pyrophosphate of magnesia obtained. | Per centage of magnesia existing as soluble salts. |
|---|---|---|
| I. 469·95 grm. | 0·1085 grm. | 0·008480 |
| II. 454·536 „ | 0·1037 „ | 0·008359 |
| | | *Mean* 0·008419 |

*G.* Determination of soda.

| Water employed. | Chloride of sodium obtained. | Per centage. | Per centage of soda in the water. |
|---|---|---|---|
| I. 35·165 grm. | 0·3360 grm. | 0·955495 | 0·505876 |
| II. 21·466 „ | 0·2050 „ | 0·954900 | 0·505450 |
| | | | *Mean* 0·505663 |

50·3975 lbs. = 22858·07843 grm. of the water were evaporated to 941·5 grm. There were obtained 7·727 grm. of precipitate, and 2242·8 grm. of filtrate, including the washings.

In the precipitate (*a*) the crenic acid was determined; in the filtrate (*b*), the iodine and extractive matter.

*H.* Determination of iodine.

91·394 grm. of the filtrate (*b*) were evaporated to dryness with carbonate of soda, the residue was digested in strong alcohol, the solution thus obtained was again evaporated, and the residue once more heated with alcohol. On the evaporation of this alcoholic extract, a small residue was obtained, which was dissolved in water. On the addition of protochloride of palladium to the clear solution, it became turbid, and after standing for some hours, deposited a blackish precipitate of protiodide of palladium, which was collected on a weighed filter, first washed with water, then with alcohol, and finally, with a little ether. It was then dried at a low temperature, and the iodine calculated from the amount obtained.

| Filtrate (*b*) employed. | Palladium salt obtained. | Per centage of iodine in the water. |
|---|---|---|
| 91·394 grm. | 0·0075 grm. | 0·000567 |

*I.* Determination of crenic acid.

| Precipitate (*a*) employed. | Copper-salt obtained. | Per centage of crenic acid in the water. |
|---|---|---|
| 1·0185 grm. | 0·0555 grm. | 0·000476 |

*K.* Determination of extractive matter.

| Filtrate (*b*) employed. | Amount of extractive matter. | Per centage in the water. |
|---|---|---|
| 68·67 grm. | 0·1805 grm. | 0·025790 |

*L.* Determination of carbonic acid.

1611·71205 cubic centimetres of water yielded 1·6615 grm. of precipitate.

| Precipitate employed. | Carbonic acid obtained. | Per centage in the precipitate. | Per centage in the water. |
|---|---|---|---|
| I. 0·5435 grm. | 0·173 grm. | 31·83 | 0·032925 |
| II. 0·6615 „ | 0·212 „ | 32·04 | |
| | | 31·935 | |

From the above analytical results the following composition of the four waters has been deduced:

| | I. Cambray chalybeate spring. | | II. Pitville strong saline water. | | III. Sulphuretted saline water, (No. 1.) Royal Old Wells. | | IV. Strong saline water, (No. 4.) Royal Old Wells. | |
|---|---|---|---|---|---|---|---|---|
| | Grm. in 100 kilogr. (litres). | Grains in an imper. gallon. | Grm. in 100 kilogr. (litres.) | Grains in an imperial gallon | Grm. in 100 kilogr. (litres). | Grains in an imperial gallon | Grm. in 100 kilogr. (litres.) | Grains in an imperial gallon |
| Sulphate of potassa | 0·683 | 0·4781 | 4·216 | 2·9512 | traces | traces | traces | traces |
| Chloride of potassium | 7·213 | 5·0491 | .. | .. | .. | .. | .. | .. |
| Sulphate of soda | .. | .. | 161·238 | 112·8666 | 334·366 | 234·0562 | 135·630 | 94·9410 |
| Chloride of sodium | 1·734 | 1·2138 | 687·419 | 481·1933 | 328·268 | 229·7876 | 843·330 | 590·3310 |
| Bromide of sodium | .. | .. | 4·704 | 3·2928 | .. | .. | .. | .. |
| Iodide of sodium | .. | .. | traces | traces | traces | traces | .. | .. |
| Carbonate of soda | 5·981 | 4·1867 | 28·783 | 20·1481 | .. | .. | .. | .. |
| Chloride of magnesium | .. | .. | .. | .. | 75·171 | 52·6197 | 11·429 | 8·0003 |
| Bromide of magnesium | .. | .. | .. | .. | .. | .. | 4·376 | 3·0632 |
| Iodide of magnesium | .. | .. | .. | .. | .. | .. | 0·623 | 0·4361 |
| Carbonate of magnesia | 6·232 | 4·3624 | 16·271 | 11·3897 | 2·817 | 1·9719 | 9·718 | 6·8026 |
| Chloride of calcium | .. | .. | .. | .. | 13·225 | 9·2575 | .. | .. |
| Bromide of calcium | .. | .. | .. | .. | 2·896 | 2·0272 | .. | .. |
| Phosphate of lime | 0·797 | 0·5579 | traces | traces | traces | traces | traces | traces |
| Carbonate of lime | 35·887 | 25·1209 | 11·003 | 7·7021 | 31·544 | 22·0808 | 24·373 | 17·0611 |
| Phosphate of sesquioxide of iron. | .. | .. | .. | .. | 0·262 | 0·1834 | .. | .. |
| Carbonate of protoxide of iron | 4·134 | 2·8938 | .. | .. | 0·857 | 0·5999 | traces | traces |
| Silicic acid | 0·954 | 0·6678 | 3·965 | 2·7755 | 1·447 | 1·0129 | 3·924 | 2·7468 |
| Apocrenic acid | 0·210 | 0·1470 | .. | .. | .. | .. | .. | .. |
| Crenic acid | 0·347 | 0·2429 | 0·513 | 0·3591 | 24·035 | 16·8245 | 0·476 | 0·3332 |
| Organic extractive matter | 0·014 | 0·0098 | 4·999 | 3·4993 | 0·033 | 0·0231 | 25·790 | 18·0530 |
| | 64·186 | 44·9302 | 923·111 | 646·1777 | 814·921 | 570·4447 | 1059·669 | 741·7683 |
| Fixed residue found by direct experiment | 64·700 | 45·2900 | 922·294 | 645·6058 | 817·493 | 572·2451 | 1059·682 | 741·7774 |
| | cubic centime. in a litre. | cubic inches in an imp. gallon. | cubic centime. in a litre. | cubic inches in an imp. gallon. | cub. centimetr. in a litre. | cubic inches in an imp. gallon. | cubic centime. in a litre. | cubic inches in an imp. gallon. |
| Amount of free carbonic acid at the stated temperatures | 62·459 | 19·919 | 58·634 | 16.254 | 117·978 | 32·705 | 91·243 | 25·294 |
| Hydrosulphuric acid | traces | traces | traces | traces | traces | traces | traces | traces |

Before entering upon the comparison of our analyses with those previously made, we may mention, that on arranging the results obtained with the saline water, it was found, that the lime and a portion of the magnesia which was not precipitated by boiling the water, must exist as carbonates held in solution by the alkaline salts. It is well known that carbonate of lime is not absolutely insoluble in water (according to experiment, 1 part of carbonate of lime requires about 10·000 parts of water), and that this solubility is increased if carbonate of ammonia and caustic ammonia be present in the water, (1 part then requiring only about 6·800 parts of ammoniacal water). We have satisfied ourselves, by direct experiment, that the solubility of carbonate of lime is much increased by the presence of chloride of sodium and sulphate of soda; at least, if we may judge from the precipitate which oxalate of ammonia produces in these solutions, the precipitate in water or ammoniacal water by the same reagent being scarcely perceptible. The slight solubility of carbonate of lime in water containing alkaline salts, makes it very desirable for the accurate determination of the alkalies, to add, after the addition of carbonate of ammonia, a few drops of oxalate of ammonia, to remove the last traces of lime, or of baryta, which have served for the separation of magnesia.

On glancing over the synoptical table, in which we have collected the results of the different analyses, we are at once struck by the small quantity of fixed constituents contained in the Cambray water, when compared with that of the other three; whilst the latter three contain between 500 and 800 grains in the imperial gallon, we find in the Cambray water not more than 64 grains, a quantity scarcely exceeding the amount of fixed constituents in common well-water. Again, we observe, quite irrelative of the amount of fixed substances, that they differ also very considerably with regard to their nature. The four waters possess an alkaline reaction; but whilst this reaction is most prominent in the Cambray and Pitville waters, which contain a considerable amount of carbonate of soda, the alkalinity of the other two is scarcely perceptible, and only becomes manifest on evaporation, arising evidently from the decomposition of the large quantity of chloride of magnesium which these waters contain. The Cambray and Pitville springs are therefore carbonated alkaline, while the others are carbonated saline waters.

Our analyses of these waters differ very considerably from all others previously published. In all the four which we examined, potassa was detected in larger or smaller quantities; of this no mention is made in any other analysis, excepting one by Scudamore, who

states, that potassa exists in small quantity in one of the waters of the Royal Old Wells.

In a paper by Dr. Daubeny* on the presence of iodine and bromine in the brine springs of England, it is stated that no bromine is found in those springs of Cheltenham which contain iodine, whilst in the Pitville spring, the only one not containing iodine, every six gallons contain about 1 grain of bromine. In three of the waters analysed by us, we found bromine in estimable quantities, accompanied always by small amounts of iodine.

The phosphoric acid has also been overlooked in these springs.

Respecting the gaseous constituents, the large quantity of carbonic acid is at once obvious, especially in the sulphuretted and saline water; it far exceeds the quantity contained in the King's Well at Bath.

Small quantities of hydrosulphuric acid were found in all the Cheltenham waters, but in none of those which we collected was it capable of being estimated. In the analyses of the old wells, published some years ago by Scudamore,† the amount of hydrosulphuric acid is stated to be not only estimable, but very considerable. Dr. Gairdner, in his work on thermal springs,‡ mentions, however, that the quantity of this gas in these waters varies exceedingly, being always much greater in rainy seasons.

The most probable view with respect to the formation of this gas seems to be the decomposition of the sulphates by the organic matter contained in the water. In support of this, we may mention that a stone bottle full of the water from Pitville, which scarcely contains a trace of hydrosulphuric acid, was found, on being opened shortly after its arrival in London, to be highly charged with this gas—which phenomenon could only arise from the presence of some particles of cork which had accidentally fallen into the water—as other quantities of the same water were kept for a great length of time in stoppered bottles without undergoing the slightest change.

Several views have been adopted to explain the formation of the mineral springs of Cheltenham. The most probable appears to be that of Sir R. Murchison, which is mentioned in his work on the Geology of Cheltenham. He supposes the springs to arise from the new red sand-stone, where they become impregnated with saline ingredients, and passing up through crevices in the lias, and through

* Philosophical Transactions, May, 1830.

† A chemical and medical report of the properties of the mineral waters of Buxton, &c., by C. Scudamore, M.D. 1820.

‡ Thermal and mineral springs, by Dr. Gairdner, 1832.

various strata of marl and clay, loaded with iron pyrites, these ingredients undergo certain chemical changes, one of which he presumes to be the formation of sulphuric acid, which combines, in its passage upwards, with various bases. He hence concludes, that those springs which are of the greatest depth, having the largest amount of strata to pass through, acquire the most valuable properties.

It is a well known fact that the strength and constitution of the Cheltenham waters are very inconstant, and that frequently, springs which have hitherto been valuable, will suddenly be deprived of so large an amount of ingredients, that the proprietors are forced to abandon them. The supply at most of the springs is limited, as is shown by the fact, that numbers of wells are sunk, in order to supply one main well properly. The late Mr. Thompson, of Montpelier, went to a very great expense in sinking a large number of deep wells, in the surrounding country, at the distance of some miles from his Spa, in order that he might obtain a proper supply. Expensive precautions have likewise been taken by the various proprietors to prevent the waters becoming adulterated by rain-water that might penetrate through the upper soil into the wells, by making the higher portions of these perfectly impermeable to moisture. It must be admitted by the most sceptic, that these facts are wholly irreconcileable with the suppositions of many people, that the Cheltenham waters are artificially impregnated by the proprietors; a supposition that has most likely arisen from the circumstance, that there is a laboratory adjoining the Montpelier Spa, where the water is evaporated, in order to obtain the salts, as also from the knowledge, that so-called Cheltenham salts are prepared artificially in that town, and by chemists all over the country.

The following is a tabular view of all the published analyses of the Cheltenham waters we have been enabled to procure:

[SEE TABLE.]

In conclusion, we cannot refrain from noticing the great readiness with which the proprietors of the various Spas furnished us with every opportunity and convenience for examining their wells and arrangements.

| | bro-of i. | Hydrio-date of soda. | Solid contents. grains in a gallon. | Free carbonic acid gas. Cubic inches in a gallon. | Free hydro-sulphuric acid gas. Cubic inches in a gall. | Authority for the analysis. |
|---|---|---|---|---|---|---|
| MONTPELL | | | | | | |
| No. 1. Saline c | ce | a trace | 387·20 | 20· | .. | Cooper. |
| No. 2. Iodurett phurretted sa | | 1·2 | 596·56 | 3·2 | 12·8 | ,, |
| No. 4. Pure sal | ce | a trace | 710·4 | 11·2 | .. | ,, |
| No. 4 A. Stron saline . . | | 2·0 | 850·00 | 12·8 | .. | ,, |
| No. 5. Iodinate saline . . | ce | 2·80 | 686·80 | 9·6 | .. | ,, |
| PITTVILL | | | | | | |
| No. 1. Strong | n of ine gall. | a trace | 366·4 | .. | .. | Daubeny. |
| ,, | ce | .. | 647·2 | 8 | .. | Daniel. |
| ,, | | a trace | 600·24 | .. | .. | Buckman. |
| ROYAL OLI | | | | | | |
| No. 1. Original | | .. | 652·08 | 1·10 | 3·53 | Scudamore. |
| No. 2. Sulphur | | .. | 670·08 | 1·15 | 4·60 | ,, |
| No. 3. Strong line . . | | .. | 537·44 | 1·5 | 1·35 | ,, |
| No. 4. Pure sal | | .. | 956.72 | .. | .. | ,, |
| No. 6. Strong line . . | | .. | 1033·6 | a large quantity | .. | ,, |
| Cambray chalyb | | .. | 64·50 | 24· | .. | Accum. |
| Sulphur spring | | .. | 520·0 | 12·0 | 20·0 | Brande & Parkes. |
| Pure saline . | | .. | 644·0 | | .. | ,, ,, |
| Chalybeate . | | .. | 590·4 | 20· | .. | ,, ,, |

REMARKS. f carbonate of protoxide of iron. It contains, besides a large impregna uld be drank immediately at the pump, when pumped up, as the hydr potassa in very small quantities, and also a trace of silex.—J. SCU

[*To face page* 32.

## III.— *Analysis of the Water of the Artesian Wells, Trafalgar Square.*

By F. A. Abel and Thos. H. Rowney, Esqrs.

ASSISTANTS AT THE ROYAL COLLEGE OF CHEMISTRY.

(Read before the Chemical Society of London, 1848.)

The deep well-water of the London Basin has been analysed by Professor Graham.* The striking feature of this analysis is the discovery of the presence of phosphoric acid, and the absence of salts of potassa.

The water which Professor Graham analysed, was taken from the deep well in the brewery of Messrs. Combe and Delafield, Long Acre. This well not descending so deep into the chalk as the Artesian Wells, in Trafalgar Square, we were induced to subject the water of the latter to an analysis in order to compare the results with those obtained by Professor Graham. The water on which we operated was taken in the beginning of October, 1847, from the shaft at the back of the National Gallery.

At a depth of about 109 feet, the water enters the shaft through a bore-hole, which passes the London clay and penetrates into the chalk. Thus the water rises from a depth of nearly 400 feet. The temperature of the water is 14·5° C. (58° Fahr.), its sp. gr. is 1000·95, the sp. gr. of distilled water being 1000.

The water is very soft, and very delicate test-papers show that it has an alkaline reaction.

A careful qualitative analysis of the water having pointed out the presence of potassa, soda, magnesia, lime, sulphuric, silicic, carbonic, hydrochloric acids, and traces of phosphoric acid, as well as a small quantity of organic matter and ammonia, the following experimental numbers were obtained by quantitative analysis.

*A.* Determination of the total amount of fixed constituents:

| | Amount of water. | Fixed residue. | Per centage. |
|---|---|---|---|
| I. | 1097·895 grm. | 1·0929 grm. | 0·09954 |
| II. | 1009·028 „ | 0·9965 „ | 0·09876 |
| | | *Mean* | 0·09915 |

* Memoirs of the Chemical Society, vol. II. p. 239.

*B.* Determination of sulphuric acid:

| | Amount of water. | Amount of sulphate of baryta. | Per centage of sulph. acid. |
|---|---|---|---|
| I. | 356·464 grm. | 0·1657 grm. | 0·01598 |
| II. | 326·303 „ | 0·1527 „ | 0·01607 |
| | | | *Mean* 0·01602 |

*C.* Determination of chlorine:

| | Amount of water. | Amount of chloride of silver. | Per centage of chlorine. |
|---|---|---|---|
| I. | 208·481 grm. | 0·1465 grm. | 0·01738 |
| II. | 339·337 „ | 0·2390 „ | 0·01741 |
| | | | *Mean* 0·01739 |

*D.* Determination of silicic acid:

| | Amount of water. | Amount of silicic acid. | Per centage. |
|---|---|---|---|
| I. | 547·155 grm. | 0·0073 grm. | 0·00133 |
| II. | 516·700 „ | 0·0067 „ | 0·00129 |
| | | | *Mean* 0·00131 |

*E.* Determination of lime:

| | Amount of water. | Amount of carbonate of lime. | Per centage of lime. |
|---|---|---|---|
| I. | 547·155 grm. | 0·0255 grm. | 0·00261 |
| II. | 516·700 „ | 0·0242 „ | 0·00262 |
| | | | *Mean* 0·002615 |

*F.* Determination of magnesia:

| | Amount of water. | Amount of pyrophosphate of magnesia. | Per centage of magnesia. |
|---|---|---|---|
| I. | 547·155 grm. | 0·0237 grm. | 0·00159 |
| II. | 516·700 „ | 0·0217 „ | 0·00153 |
| | | | *Mean* 0·00156 |

*G.* Determination of the alkalies:

| | Amount of water. | Amount of chlorides of potassium and sodium. | Per centage. |
|---|---|---|---|
| I. | 245·307 grm. | 0·2015 grm. | 0·08206 |
| II. | 219·182 „ | 0·1920 „ | 0·08759 |
| | Amount of water. | Amount of chloride of potassium and platinum. | Per centage of potassa. |
| I. | 245·307 grm. | 0·1277 grm. | 0·01008 |
| II. | 219·182 „ | 0·1255 „ | 0·01101 |
| | | | *Mean* 0·01055 |

| Amount of water. | Amount of chloride of sodium. | Per centage of soda. |
|---|---|---|
| I. 245·307 grm. | 0·16255 grm. | 0·03467 |
| II. 219·182 „ | 0·15380 „ | 0·03713 |
| | | *Mean* 0·03590 |

*H.* Determination of carbonic acid:

The carbonic acid was determined by precipitating a known volume of water by a mixture of chloride of calcium and ammonia at the well. 2134·0254 cubic centimetres of water, in this manner, yielded 1·3397 grm. of precipitate, in which the carbonic acid was determined.

| Amount of precipitate. | Amount of carbonic acid. | Per centage in the precipitate. |
|---|---|---|
| I. 0·3656 grm. | 0·117 grm. | 32·002 |
| II. 0·3679 „ | 0·118 „ | 32·070 |
| | | *Mean* 32·036 |

The whole amount of precipitate accordingly contained 0·4297 grm. carbonic acid, representing a per centage of 0·02013 carbonic acid in the water.

*I.* Determination of the total amount of phosphoric acid:

A known quantity of water was evaporated to dryness, the residue obtained was fused in a platinum capsule, the fused mass digested with water, the solution filtered, and the phosphoric acid determined therein as pyrophosphate of magnesia.

| Amount of water. | Amount of pyrophosphate of magnesia. | Per centage of phosphoric acid in the water. |
|---|---|---|
| 1002·208 grm. | 0·0037 grm. | 0·000233 |

For the determination of the small amount of phosphoric acid, in combination with lime, of organic matter existing in the water in the different forms designated as apocrenic and crenic acids, and of extractive matter,

3·631712 kilogrammes of the water were evaporated to 306·923 grm. yielding a precipitate (*a*), insoluble in water, of . . 2·899 „
the solution (*b*) along with the washings amounting to 569·306 „

*K.* Determination of the phosphoric acid in combination with lime:

| Amount of precipitate (*a*) | Amount of pyrophosphate of magnesia. | Per centage of phosphoric acid in the water, combined with lime. |
|---|---|---|
| 0·6925 grm. | 0·0032 grm. | 0·0000234 |

*L.* Determination of the organic matter:

0·6100 grm. of precipitate (*a*) was extracted with potassa, the alkali was saturated with acetic acid, and acetate of copper added; there was obtained, after standing for some time,

0·0189 grm. of a brown precipitate of apocrenate of copper, corresponding to 0·0001414 per cent of apocrenic acid in the water.

The filtrate form this precipitate, on boiling with excess of carbonate of ammonia, yielded:

0·0567 grm. of a greenish precipitate of crenate of copper, corresponding to 0·000196 per cent of crenic acid in the water.

For the determination of what is usually called extractive matter: 189·50 grm. of the solution (*b*) were evaporated with carbonate of soda, the residue obtained was dried, weighed, and afterwards ignited; it lost 0·1165 grm. corresponding to:

0·00096 per cent of extractive matter in the water.

From these analytical results, the following composition of the water is deduced:

| | Grammes in 100 kilogrammes. (litres.) | Grains in an imperial gallon. (70,000 grs.) |
|---|---|---|
| Carbonate of lime | 4·65000 | 3·255000 |
| Phosphate of lime | 0·04863 | 0·034041 |
| Carbonate of magnesia | 3·22000 | 2·254000 |
| Sulphate of potassa | 19·53000 | 13·671000 |
| Sulphate of soda | 12·49900 | 8·749300 |
| Chloride of sodium | 28·65500 | 20·058500 |
| Phosphate of soda | 0·41600 | 0·291000 |
| Carbonate of soda | 25·78400 | 18·048800 |
| Silicic acid | 1·31000 | 0·971000 |
| Apocrenic acid | 0·14100 | 0·098700 |
| Crenic acid | 0·19600 | 0·137200 |
| Extractive matter | 0·96000 | 0·672000 |
| | 97·40963 | 68·240541 |

The amount of fixed residue obtained by direct experiment was:

in 100 kilogrammes . . . . 99·150 grm.;
in an imperial gallon . . . . 69·405 grs.

According to the experiments detailed above, one litre of water contains 30·3864 cubic centimetres of free carbonic acid at the temperature 14·5° C. (58·1° F.); one imperial gallon contains, therefore, 8·4235 cubic inches.

In order to ascertain whether the water loses a portion of carbonic acid in being pumped up, a determination of this gas was made in some of the water, as it issued from the mouth of the force-pump in the works:

| Water employed. | Precipitate obtained. | Per centage of carbonic acid in the water. |
|---|---|---|
| 1067·012 cubic centimetres | 0·2103 grm. | 0·01971 |

After deducting the amount of carbonic acid in combination with lime, magnesia, and soda, from the per centage obtained above, we have remaining a quantity corresponding to 28·153 cubic centimetres in a litre, or 7·805 cubic inches in an imperial gallon at 14·5° C. (58·1° F.)

From these results, it is evident that a small quantity of carbonic acid is lost by the process of pumping.

To ascertain the amount of matter precipitated by boiling the water, known quantities were submitted to strong ebullition for some time, the precipitates formed were collected on tared filters, dried and weighed.

| Water employed. | Precipitate formed. | Per centage. |
|---|---|---|
| 439·608 grm. | 0·0392 grm. | 0·00892 |
| 357·393 „ | 0·0320 „ | 0·00895 |
| | | *Mean* 0·008935 |

The mean quantity obtained corresponds to 6·2545 grs. in an imperial gallon, or 0,08935 grm. in a litre.

The preceding analysis shows that the constituents of the water of the Artesian Wells, in Trafalgar Square, are essentially the same as those of the water from the well in Messrs. Combe and Delafield's brewery. There is only one point in which the two waters materially differ in composition. The water which Professor Graham analysed, and which, as already mentioned, comes from a higher stratum, was found to contain no potassa salts, whilst these were invariably present in the waters of Trafalgar Square. In order to preclude the possibility of error, the water which we employed for testing was collected at different periods.

M. Payen * found that the water of the Artesian Well at Grenelle contains a considerable amount of sulphate of potassa and chloride of potassium, so that it would appear that potassa salts are characteristic of the waters from the deeper strata.

The water analysed by us did not contain a trace of iron.

The presence of phosphoric acid, first pointed out by Professor Graham in deep well-water, could be easily ascertained in the Tra-

* Annales de Chimie et de Physique, 3ème sér. tom. i. p. 381.

falgar Square water by the method indicated by that chemist; in fact, on evaporating the water to dryness, and gently igniting the residue, the phosphoric acid, existing partly in combination with lime and partly with soda, is obtained altogether in the form of a soda-salt, the solution of which deposits the yellow tribasic silver-salt on the addition of nitrate of silver.

The large amount of organic matter contained in the deep well-water is very remarkable, while the quantity observed in the water of a higher stratum seems to have been very trifling. It evidently arises from the remains of organized beings which have invariably been found in the chalk.

With reference to the quantities in which the different constituents are present, it will be observed, on comparison, that the total amount of fixed constituents is somewhat different (56·80 and 68·24), whilst very considerable deviations are perceptible in the quantities of the various constituents. The most striking difference is observed in the quantities of sulphate of soda contained in the two waters.

In conclusion, we give a tabular view for the comparison of the water analysed by Professor Graham and the Trafalgar Square water, to which we annex the results obtained by M. Payen from the analysis of the water of Grenelle.

| | Wells at Messrs. Combe & Delafield. | Trafalgar Square wells. | Grenelle. |
|---|---|---|---|
| | Grains in an imperial gallon. | | |
| Carbonate of lime | 6·18 | 3·2550 | 4·7600 |
| Phosphate of lime | 0·19 | 0·0340 | — |
| Phosphate of sesquioxide of iron | 0·24 | — | — |
| Carbonate of magnesia | 1·08 | 2·2540 | 0·9940 |
| Sulphate of potassa | — | 13·6710 | 0·8600 |
| Chloride of potassium | — | — | 0·7630 |
| Bicarbonate of potassa | — | — | 2·0720 |
| Sulphate of soda | 24·25 | 8·7493 | — |
| Chloride of sodium | 12·74 | 20·0585 | — |
| Phosphate of soda | — | 0·2910 | — |
| Carbonate of soda | 11·68 | 18·0488 | — |
| Silicic acid | 0·44 | 0·9710 | 0·3990 |
| Apocrenic acid | — | 0·0987 | — |
| Crenic acid | — | 0·1372 | — |
| Extractive matter | — | 0·6720 | — |
| Yellow substance | — | — | 0·0014 |
| Organic matter (nitrogenous) | — | — | 0·0138 |
| | 56·80 | 68·2405 | 9·8632 |

The purity of the water of Grenelle is most remarkable; the amount of fixed constituents being only about $\frac{1}{7}$th of that which is found in the London waters.

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## IV.—*Analysis of the Thames Water.*

By George Frederick Clark, Esq.

(Read before the Chemical Society of London, 1848.)

It can scarcely be doubted that the composition of the Thames water has been repeatedly the subject of chemical investigation; it appears, nevertheless, that no detailed analysis of it has been published, although an accurate knowledge of its nature must be very desirable, on account of the great variety of processes for which this water is daily employed in our metropolis. It is evident that a single analysis cannot possibly afford anything like a satisfactory idea of the composition of the water of a river like the Thames. For this purpose, it is necessary to investigate it at different localities and at different periods; in a word, a series of analyses must be performed. As one of this series, suggested by Dr. Hofmann to several of his pupils, I undertook the analysis of the water as it is found before it has been polluted by the London drains and sewers. The water was accordingly collected on the 16th of December, 1847, from the middle of the river, two hours after high-tide, in the neighbourhood of Twickenham, which is fourteen miles from London Bridge.

The temperature of the water was $9^{0}{\cdot}5$ cent. or $49^{0}{\cdot}1$ Fahr.

The temperature of the air being $13^{0}$ cent. or $55^{0}{\cdot}4$ Fahr.

The specific gravity of the water was 1·0003.

A careful qualitative analysis pointed out the presence of potassa, soda, lime, magnesia, iron, alumina, chlorine, sulphuric acid, silicic acid and organic matter; a trace of phosphoric acid was also observed.

Bromine and iodine could not be detected in the water, even after considerable concentration. The quantitative analysis gave the following results:

*A.* Determination of the total amount of fixed constituents:

| | Amount of water employed. | Amount obtained. | Per centage. |
|---|---|---|---|
| I. | 1182·582 grm. | 0·378 grm. | 0·0319639 |
| II. | 1000·208 „ | 0·323 „ | 0·0322932 |
| | | *Mean* | 0·03212855 |

*B.* Determination of sulphuric acid:

| | Amount of water employed. | Amount of sulphate of baryta obtained. | Per centage of sulphuric acid. |
|---|---|---|---|
| I. | 610·293 grm. | 0·350 grm. | 0·0024265 |
| II. | 581·275 „ | 0·330 „ | 0·0024294 |
| | | *Mean* | 0·0024279 |

*C.* Determination of chlorine:

| | Amount of water employed. | Amount of chloride of silver obtained. | Per centage of chlorine. |
|---|---|---|---|
| I. | 610·65 grm. | 0·039 grm. | 0·0015794 |
| II. | 580·35 „ | 0·083 „ | 0·0016192 |
| | | *Mean* | 0·0015993 |

*D.* Determination of silicic acid:

| | Amount of water employed. | Amount of silicic acid obtained. | Per centage of silicic acid. |
|---|---|---|---|
| I. | 1182·582 grm. | 0·0045 grm. | 0·0003805 |
| II. | 1000·208 „ | 0·0040 „ | 0·0003999 |
| | | *Mean* | 0·0003902 |

*E.* Determination of lime and magnesia:

| | | Amount of water employed. | Amount of carbonate of lime obtained. | Per centage of lime. |
|---|---|---|---|---|
| *a.* | I. | 1000·598 grm. | 0·2096 grm. | 0·0117305 |
| | II. | 906·002 „ | 0·1899 „ | 0·0117377 |
| | | | *Mean* | 0·0117341 |

Determination of magnesia in the filtrate from the oxalate of lime:

| | | Amount of water employed. | Amount of pyrophosphate of magnesia obtained. | Per centage of magnesia. |
|---|---|---|---|---|
| *b.* | I. | 1000·698 grm. | 0·0195 grm. | 0·0007140 |
| | II. | 906·002 „ | 0·0175 „ | 0·0007077 |
| | | | *Mean* | 0·0007108 |

*F.* Determination of the alkalies:

| | | Amount of water employed. | Amount of mixed chlorides obtained. |
|---|---|---|---|
| *a.* | I. | 1000·000 grm. | 0·0305 grm. |
| | II. | 1184·304 „ | 0·0390 „ |

Determination of potassa:

| | Amount of water employed. | Amount of bichloride of platinum and potassium obtained. | Per centage of potassa. |
|---|---|---|---|
| *b.* | I. 1000·000 grm. | 0·0265 grm. | 0·0005105 |
| | II. 1184·304 „ | 0·0320 „ | 0·0005205 |
| | | *Mean* | 0·0005155 |

Determination of soda:

| | Amount of water employed. | Amount of chloride of sodium obtained. | Per centage of soda. |
|---|---|---|---|
| *c.* | I. 1000·000 grm. | 0·0022407 grm. | 0·0011867 |
| | II. 1184·304 „ | 0·0024679 „ | 0·0013071 |
| | | *Mean* | 0·0012469 |

31963·6 grm. of the water were evaporated down to 574·475 grm. The precipitate which was formed and separated weighed 5·558 grm.

Determination of organic matter in the filtrate:

| Amount of filtrate employed. | Amount of organic matter burnt off. | Per centage upon the whole amount of water. |
|---|---|---|
| I. 81·520 grm. | 0·148 grm. | 0·0032629 |
| II. 129·839 „ | 0·236 „ | 0·0032668 |
| | *Mean* | 0·0032648 |

Determination of organic matter in the precipitate:

| Amount of precipitate employed. | Amount of organic matter burnt off. | Per centage upon the whole amount of water. |
|---|---|---|
| I. 0·0925 grm. | 0·0090 grm. | 0.0016918 |
| II. 0·1565 „ | 0·0155 „ | 0·0017221 |
| | *Mean* | 0·0017069 |

Determination of carbonic acid:

At the time of collecting the water, a syphon capable of containing 0·557 cubic centimetres of distilled water was filled three times, and discharged into a bottle containing chloride of calcium and ammonia; the precipitate which was formed weighed, when dry, 0·937 grm.

| Amount of precipitate employed. | Amount of carbonic acid evolved. | Amount calculated on the whole precipitate. |
|---|---|---|
| I. 0·4175 grm. | 0·136 grm. | 0·3052263 grm. |
| II. 0·4585 „ | 0·165 „ | 0·3167611 „ |
| | *Mean* | 0·3109937 „ |

Per centage in the water 0·01860565.

From the preceding experiments, the ingredients are found to exist in the following proportions:

| | In 100 litres, Grammes. | In a gallon, Grains. |
|---|---|---|
| Sulphate of potassa | 0·9542 | 0·66794 |
| Sulphate of soda | 2·8573 | 2·00011 |
| Sulphate of lime | 0·6439 | 0·45073 |
| Chloride of calcium | 2·5003 | 1·75021 |
| Carbonate of lime | 18·2278 | 12·75946 |
| Carbonate of magnesia | 1·4673 | 1·02711 |
| Silicic acid | 0·3902 | 0·27314 |
| Phosphoric acid | traces | traces |
| Alumina | traces | traces |
| Carbonate of protoxide of iron | traces | traces |
| Soluble organic matter | 3·2648 | 2·28536 |
| Insoluble organic matter | 1·7069 | 1·19483 |
| | 32·0127 | 22·40889 |
| Direct determination of fixed constituents | 32·1285 | 22·48995 |

Having deducted from the per centage of carbonic acid the portion in combination with lime and magnesia, the per centage of free carbonic acid was found to be 0·0098289, corresponding to 5134·393 cubic centimetres in 100 litres, or 14·233 cubic inches in an imperial gallon.

The iron and aluminum were not separated; but both were determined in the state of sesquioxides.

The mean result of two experiments gave 0·00001335 per cent of the mixed sesquioxides.

From the foregoing analysis, it appears that the principal ingredient in Thames water in the neighbourhood of London is carbonate of lime, held in solution by free carbonic acid, and which would therefore be deposited upon continued boiling.

I cannot conclude this paper, without mentioning the attention and kindness of my friend, Dr. Hofmann, in affording me every facility for the prosecution of the above analysis.

## V.—*Analysis of the Ashes of the Orange-Tree* (Citrus aurantium).

By Thomas H. Rowney and Henry How, Esqrs.

(Read before the Chemical Society of London, April 5th, 1847).

For the materials used in the following analyses we are indebted to the kindness of Mr. Da Cumara, who had sent it over for investigation from his plantations on the island of St. Michel, being desirous to become acquainted with the mineral constituents of the orange-tree, which forms the principal wealth of his country. The analyses were performed under the direction of Dr. Hofmann in the laboratory of the Royal College of Chemistry.

To prepare the ashes in a fit state for analysis, the different parts of the plant were heated in an inclined, open Hessian crucible, until the carbon was consumed.* The ashes thus obtained were mixed with a small quantity of protoxide of mercury, and ignited a second time in a platinum capsule over a spirit-lamp, in order to reproduce the sulphates, which in the former process had been reduced to sulphides.

The same quantity of ash served to determine potassa and soda, sulphuric and phosphoric acids, phosphate of sesquioxide of iron, lime and magnesia, silicic acid and accidental sand and charcoal. For this purpose, the hydrochloric acid solution was evaporated to dryness, gently ignited and extracted with hydrochloric acid. The solution thus obtained was divided into different parts.

The first portion served for the determination of the potassa and soda. For this purpose the acids, lime, magnesia, &c., were removed by baryta, the excess of baryta by carbonate of ammonia, and the ammoniacal salts by gentle ignition. The residue, potassa and soda, were estimated partly by separating them by means of bichloride of platinum (analyses of the ashes of the root and seed) and partly by the indirect method, namely, by converting the mixed chlorides into sulphates, weighing these and ascertaining the amount of sulphuric acid by means of chloride of barium (analyses of the stem, leaves and fruit).

In the second portion, sulphuric and phosphoric acids were determined, the former as sulphate of baryta, the latter by neutralizing the filtrate from the former with ammonia and precipitating the phosphoric acid by means of sesquichloride of iron and acetate of

* To obtain the ash of the fruit, the oranges were cut into slices, and after separation of the seed, dried on the sand-bath in a covered porcelain dish, and then burnt in a crucible.

potassa. This precipitate was dissolved in hydrochloric acid, a sufficient quantity of tartaric acid was added, and the phosphoric acid estimated in the form of pyrophosphate of magnesia, by precipitating with ammonia, chloride of ammonium and sulphate of magnesia. The latter precipitate frequently containing a small quantity of iron, was redissolved in hydrochloric acid, and after the addition of some tartaric acid reprecipitated by ammonia. A third portion served for the estimation of phosphate of sesquioxide of iron, lime and magnesia. For this purpose the liquid was neutralized with ammonia, some acetate of potassa was added, and the solution strongly acidulated with acetic acid, in order to keep the phosphate of lime, which might be precipitated, in solution; on heating, the phosphate of sesquioxide of iron subsides, from which the sesquioxide of iron was calculated according to the formula $2Fe_2O_3$, $3PO_5$. From the filtrate, the lime was precipitated by means of oxalate of ammonia, and after the separation of the lime, the magnesia by phosphate of soda. Chlorine and carbonic acid were determined in separate portions of the ash. In this manner the following experimental numbers were obtained:—

| | Roots. | | Stem. | | Leaves. | | Fruit. | | Seed. | |
|---|---|---|---|---|---|---|---|---|---|---|
| | I. | II. | I. | II. | I. | II. | I. | II. | I. | II. |
| | grm. | grm. | grm. | grm. | grm. | grm. | grm. | grm. | grm. | grm. |
| Quantity of ash employed for the general analysis | 2·9360 | 3·0700 | 3·5800<br>3·2350<br>4·6265 | 3·277 | 4·3040 | 4·653 | 3·7490 | 3·5415 | 1·3620 | 2·3440 |
| Whole amount of the hydrochloric acid solution | 164·6340 | 154·0590 | 229·9560<br>222·6830 | 139·376 | 202·6960 | 171·503 | 207·5200 | 169·2730 | 171·1000 | 181·4500 |
| Hydrochloric acid solution for the alkalies . . | 21·3200 | 33·0500 | 23·2260 | 22·940 | 28·9130 | 20·422 | 20·7160 | 23·8680 | 41·1900 | 39·9480 |
| Hydrochloric acid solution for sulphuric and phosphoric acids . . | 24·9890 | 35·4420 | 39·3930<br>27·4560 | 25·990<br>16·180 | 23·6160 | 22·574 | 33·0130 | 18·2200 | 25·6300 | 34·2880 |
| Hydrochloric acid solution for lime, magnesia, &c. | 31·9590<br>25·6860 | 39·1550 | 38·5060<br>36·6930 | 26·331<br>25·827 | 22·8300<br>21·5500 | 24·324 | 27·3560<br>21·7160 | 22·5680 | 23·9450 | 27·3910 |
| Quantity of ash employed for the estimation of chlorine . . . | 1·4955 | 1·2235 | 1·1060 | 1·291 | 2·1230 | 1·927 | 1·9825 | 1·4595 | 0·8270 | 0·6255 |
| Quantity of ash employed for the estimation of carbonic acid . . . | 0·8400 | — | 0·8840 | — | 1·5330 | 1·619 | 1·7660 | 1·5275 | 0·5850 | — |
| Quantity of the plant dried at 100° C. for the estimation of the amount of ash . . . . | 1·7175 | — | 1·1280 | — | 1·9892 | — | 3·5450 | — | 3·7825 | — |

| | Roots. | | Stem. | | Leaves. | | Fruit. | | Seed. | |
|---|---|---|---|---|---|---|---|---|---|---|
| | I. | II. | I. | II. | I. | II. | I. | II. | I. | II. |
| | grm. | grm. | grm. | grm. | grm. | grm. | grm. | grm. | grm. | grm. |
| Silicic acid | 0·0405 | 0·0445 | 0·0330 | 0·0437 | 0·1580 | 0·176 | 0·0115 | 0·0135 | 0·0140 | 0·0225 |
| Sand and charcoal | 0·0125 | 0·0195 | 0·0120 | 0·0070 | 0·0105 | 0·010 | 0·0635 | 0·0575 | 0·0785 | 0·1325 |
| Mixed chlorides of potassium and sodium | 0·8185 | 0·8460 | — | — | — | — | — | — | 0·7913 | — |
| Bichloride of platinum and potassium | 1·9089 | — | — | — | — | — | — | — | 2·4861 | 4·2940 |
| Chloride of sodium | 0·2355 | 0·2420 | — | — | — | — | — | — | 0·0321 | 0·0520 |
| Mixed sulphates of the alkalies | — | — | 0·7772 | 0·7840 | 1·4091 | 1·511 | 2·8349 | 2·7127 | — | — |
| Sulphuric acid contained in the sulphates of the alkalies | — | — | 0·3772 | 0·3790 | 0·6863 | 0·739 | 1·3914 | 1·3330 | — | — |
| Sulphate of baryta for sulphuric acid | 0·3946 | 0·4200 | 0·3677 | 0·3620 | 0·4205 | 0·741 | 0·3143 | 0·3028 | 0·1769 | 0·3060 |
| Pyrophosphate of magnesia for phosphoric acid | 0·5007 | 0·5300 | 0·7244 | 0·7300 | 0·1673 | 0·190 | 0·5060 | 0·4830 | 0·4372 | 0·7546 |
| Phosphate of sesquioxide of iron | 0·0566 | 0·5880 | 0·0358 | 0·0375 | 0·0355 | 0·049 | 0·0303 | 0·0300 | 0·0214 | 0·0397 |
| Carbonate of lime | 2·1059 | 2·2100 | 3·7565 | 2·6900 | 3·3296 | 3·610 | 1·2858 | 1·1910 | 0·4037 | 0·6970 |
| Pyrophosphate of magnesia for magnesia | 0·4454 | 0·4700 | 0·6675 | 0·4690 | 0·5282 | 0·547 | 0·6545 | 0·5900 | 0·2929 | 0·4809 |
| Chloride of silver | 0·0370 | 0·0275 | 0·0055 | 0·0080 | 0·2640 | 0·245 | 0·1425 | 0·1110 | 0·0160 | 0·0105 |
| Carbonic acid | 0·1600 | — | 0·1460 | — | 0·3560 | 0·372 | 0·3600 | 0·3090 | 0·0400 | — |
| Amount of ash left on incineration | 0·0770 | — | 0·0310 | — | 0·2732 | — | 0·1400 | — | 0·1250 | — |

These numbers correspond to the following per centage Composition:

ANALYSIS OF THE ASHES OF THE ROOT. COMPOSITION DIRECTLY FOUND.

Amount of ashes left by 100 parts of the root . . 4·48.

| | I. | II. | Mean. |
|---|---|---|---|
| Potassa . . . . | 12·54 | 12·40 | 12·47 |
| Soda . . . . . | 3·72 | 3·57 | 3·64 |
| Lime . . . . . | 40·16 | 40·31 | 40·23 |
| Magnesia . . . | 5·55 | 5·60 | 5·57 |
| Sesquioxide of iron | 0·83 | 0·82 | 0·83 |
| Chloride of sodium | 1·01 | 0·91 | 0·95 |
| Phosphoric acid . | 10.80 | 10·93 | 10·86 |
| Sulphuric acid . . | 4·61 | 4·76 | 4·68 |
| Silicic acid . . . | 1·38 | 1·45 | 1·42 |
| Carbonic acid . . | 19·04 | 19·04 | 19·04 |
| Sand and charcoal . | 0·42 | 0·63 | 0·53 |
| | 100·06 | 100·37 | 100·22 |

Per centage of the ash after deduction of the unessential constituents, carbonic acid, sand and charcoal:

| | |
|---|---|
| Potassa . . . . . | 15·43 |
| Soda . . . . . | 4·52 |
| Lime . . . . . | 49·89 |
| Magnesia . . . . | 6·91 |
| Sesquioxide of iron . | 1·02 |
| Chloride of sodium . | 1·18 |
| Phosphoric acid . . | 13·47 |
| Sulphuric acid . . | 5·78 |
| Silicic acid . . . | 1·75 |
| | 100·00 |

ANALYSIS OF THE ASHES OF THE STEM.

Amount of ashes left by 100 parts of the stem . . 2·74

| | I. | II. | Mean. |
|---|---|---|---|
| Potassa . . . . | 9·66 | 9·73 | 9·69 |
| Soda . . . . . | 2·61 | 2·47 | 2·54 |
| Lime . . . . . | 45·46 | 45·96 | 45·71 |
| Magnesia . . . | 5·28 | 5·24 | 5·26 |
| Sesquioxide of iron | 0·48 | 0·48 | 0·48 |
| Chloride of sodium | 0·19 | 0·24 | 0·21 |
| Phosphoric acid . | 14·18 | 14·17 | 14·17 |
| Sulphuric acid . . | 3·90 | 3·79 | 3·84 |
| Silicic acid . . . | 0·92 | 1·14 | 1·03 |
| Carbonic acid . . | 16·51 | 16·50 | 16·50 |
| Sand and charcoal | 0·33 | 0·21 | 0·27 |
| | 99·52 | 99·93 | 99·70 |

| | |
|---|---|
| Potassa | 11·69 |
| Soda | 3·07 |
| Lime | 55·13 |
| Magnesia | 6·34 |
| Sesquioxide of iron | 0·57 |
| Chloride of sodium | 0·25 |
| Phosphoric acid | 17·09 |
| Sulphuric acid | 4·64 |
| Silicic acid | 1·22 |
| | 100·00 |

ANALYSIS OF THE ASHES OF THE LEAVES.

Amount of ashes left by 100 parts of the leaves . . 13·73

| | I. | II. | Mean. |
|---|---|---|---|
| Potassa | 12·87 | 12·48 | 12·67 |
| Soda | 1·22 | 1·38 | 1·30 |
| Lime | 43·32 | 43·44 | 43·38 |
| Magnesia | 4·49 | 4·30 | 4·39 |
| Sesquioxide of iron | 0·36 | 0·44 | 0·40 |
| Chloride of sodium | 5·08 | 5·17 | 5·12 |
| Phosphoric acid | 2·46 | 2·58 | 2·52 |
| Sulphuric acid | 3·35 | 3·47 | 3·41 |
| Silicic acid | 3·67 | 3·78 | 3·72 |
| Carbonic acid | 23·22 | 22·97 | 23·09 |
| Sand and charcoal | 0·24 | 0·21 | 0·23 |
| | 100·28 | 100·22 | 100·23 |

| | |
|---|---|
| Potassa | 16·51 |
| Soda | 1·68 |
| Lime | 56·38 |
| Magnesia | 5·72 |
| Sesquioxide of iron | 0·52 |
| Chloride of sodium | 6·66 |
| Phosphoric acid | 3·27 |
| Sulphuric acid | 4·43 |
| Silicic acid | 4·83 |
| | 100·00 |

ANALYSIS OF THE ASHES OF THE FRUIT.

Amount of ashes left by 100 parts of the fruit . . 3.94

| | I. | II. | Mean. |
|---|---|---|---|
| Potassa . . . . | 28·21 | 28·32 | 28·26 |
| Soda . . . . . | 8·73 | 8·99 | 8·86 |
| Lime . . . . . | 19·20 | 18·83 | 19·02 |
| Magnesia . . . | 6·39 | 6·14 | 6·26 |
| Sesquioxide of iron | 0·35 | 0·36 | 0·35 |
| Chloride of sodium | 2·93 | 3·09 | 3·02 |
| Phosphoric acid . | 8.55 | 8·64 | 8·59 |
| Sulphuric acid . . | 2·88 | 2·93 | 2·90 |
| Silicic acid . . . | 0·31 | 0·38 | 0·34 |
| Carbonic acid . . | 20·38 | 20·22 | 20·30 |
| Sand and charcoal | 1·69 | 1·62 | 1·65 |
| | 99·62 | 99·52 | 99·55 |

| | |
|---|---|
| Potassa . . . . . | 36·42 |
| Soda . . . . . | 11·42 |
| Lime . . . . . | 24.52 |
| Magnesia . . . . | 8·06 |
| Sesquioxide of iron . | 0·46 |
| Chloride of sodium . | 3·87 |
| Phosphoric acid . . | 11·07 |
| Sulphuric acid . . | 3·74 |
| Silicic acid . . . | 0·44 |
| | 100·00 |

ANALYSIS OF THE ASHES OF THE SEED.

Amount of ashes left by 100 parts of the seed . . 3·30

| | I. | II. | Mean. |
|---|---|---|---|
| Potassa . . . . | 35·22 | 35·29 | 35.26 |
| Soda . . . . . | 0.77 | 0·84 | 0·81 |
| Lime . . . . . | 16·59 | 16·65 | 16·62 |
| Magnesia . . . | 7·87 | 7·51 | 7·69 |
| Sesquioxide of iron | 0·68 | 0·72 | 0·70 |
| Chloride of sodium | 0·77 | 0·67 | 0·72 |
| Phosphoric acid . | 20·33 | 20·39 | 20·36 |
| Sulphuric acid . . | 4·46 | 4·48 | 4·47 |
| Silicic acid . . . | 1·02 | 0·96 | 0·99 |
| Carbonic acid . . | 6·83 | 6·83 | 6.83 |
| Sand and charcoal . | 5·76 | 5·78 | 5·77 |
| | 100·30 | 100·12 | 100·22 |

| | |
|---|---|
| Potassa . . . . | 40·28 |
| Soda . . . . | 0·92 |
| Lime . . . . | 18·97 |
| Magnesia . . . | 8·74 |
| Sesquioxide of iron | 0·80 |
| Chloride of sodium | 0·82 |
| Phosphoric acid . | 23·24 |
| Sulphuric acid . | 5·10 |
| Silicic acid . . . | 1·13 |
| | 100·00 |

The preceding analyses furnish a new confirmation of the fact first observed by De Saussure, namely, that the largest amount of mineral constituents is deposited in those parts of the plant in which the process of assimilation appears to be most active. While the ash left by the root, stem, fruit, and seed did not exceed from 3 to 4 per cent., the leaves left not less than 13 per cent. of fixed residue on incineration.

Regarding the composition of the different ashes, the great amount of carbonic acid found in the ashes of the root, the stem, and the fruit is at once obvious; proving that not only the fruit, but also the roots and stem, contain a large quantity of organic acids.

From the composition of the ashes of the root, the stem, and the leaves, the orange-tree belongs decidedly to the lime plants. In these three ashes the joint amount of lime and magnesia exceeds the quantity of the rest of the mineral constituents. In the ashes of the fruit and seed, however, the alkalies are as prevalent as they have been found in analogous cases. The amount of phosphoric acid (23·24) in the ash of the seed is considerable, as might be expected, still it is inferior to the quantities (34·81 and 42·02) which Mr. Souchay found on analysing the seeds of the citron (*Citrus Medica*) and quince-trees (*Pyrus Cydonia*). Nevertheless the ash of the orange-seed is very analogous in composition to the ashes of the last-mentioned seeds, as may be easily seen on comparing their analysis.*

* Liebig's Annals, LIV, p. 343.

## VI.—*Analysis of the Bohemian Glass as found in the Combustion Tubes employed in Organic Analysis.*

By Thomas Rowney, Esq.

(Read before the Chemical Society of London, Dec. 21st. 1846.)

The difficultly fusible variety of Bohemian glass has been repeatedly the subject of chemical investigation. We are indebted to Berthier,* Dumas,† Gras,‡ and lately Peligot, for an analysis of this substance. The glass analysed by these chemists was of the kind usually employed in the manufacture of Bohemian goblets, an art in which Bohemia has excelled for centuries.

It appeared desirable to compare with the results of these analyses the composition of the glass which is used in the combustion of organic substances, and which likewise is chiefly manufactured in Bohemia. The properties most valued in this variety of glass are essentially different from those sought for in other kinds, and it was to be expected that this material, which has so greatly contributed to the progress of organic chemistry, and upon which the German manufacturers have of late bestowed so much attention, would also show some marked peculiarity of composition.

The following analysis was made in the laboratory of the Royal College of Chemistry. The glass was selected from the stock of the laboratory, recently imported from Germany, and which numerous trials had proved to be of first-rate quality. The tubes, though perfectly tractable in an energetic blow-pipe flame, scarcely altered their form during the longest combustion in a strong charcoal fire; they never cracked during the process, even on suddenly increasing the temperature, and not uncommonly the same tube could be employed repeatedly in analysis.

A careful qualitative examination of the specimen having proved the presence of silicic acid, lime, sesquioxide of iron, alumina, oxide of manganese, magnesia, soda and potassa, the quantitative determination was proceeded with.

### *a.* DETERMINATION OF SILICIC ACID.

The finely-powdered glass was ignited with carbonate of soda, treated with hydrochloric acid in excess, evaporated to dryness, once more ignited and digested with hydrochloric acid, after which all the

* Gmelin's Handbuch, vol. II, 366.

† Dumas' Traité de Chimie, vol. II, 528. ‡ Ibid.

silicic acid remained insoluble; it was collected on a filter, washed, ignited, and weighed.

I. 2·1890 grm. of glass gave 1·5946 grm. silicic acid.
II. 2·1284 grm. of glass gave 1·5628 grm. silicic acid.

*b.* DETERMINATION OF LIME.

The acid filtrate, from the silicic acid, was neutralized by ammonia, then slightly acidulated with acetic acid and precipitated by oxalate of ammonia, and the oxalate of lime converted into carbonate in the usual manner.

I. 2·1890 grm. of glass gave 0·4203 grm. of carbonate of lime.
II. 2·1284 grm. of glass gave 0·3843 grm. of carbonate of lime.

*c.* DETERMINATION OF ALUMINA AND SESQUIOXIDE OF IRON.

To the liquid filtered from the precipitate of oxalate of lime (*b*), containing a large quantity of chloride of ammonium, ammonia was added in excess, by which alumina and sesquioxide of iron were precipitated, oxide of manganese and magnesia being retained in solution. The joint precipitate of alumina and sesquioxide of iron was collected, washed, ignited and weighed; then dissolved in hydrochloric acid and thrown down with potassa, which kept the alumina in solution. The precipitate of sesquioxide of iron (thus obtained), once more dissolved in hydrochloric acid and reprecipitated by ammonia, was now collected, ignited, and weighed; the difference in the amount of the two weighings gave the amount of the alumina thus:

2·1890 grm. of glass gave 0·0096 grm. of mixed oxides and 0·0029 grm. of sesquioxide of iron; the difference, 0·0067 grm., is the amount of alumina.

*d.* DETERMINATION OF OXIDE OF MANGANESE.

This oxide was thrown down by carbonate of soda as carbonate of manganese, from the filtrate, separated from the oxide of iron and alumina (*c*); the precipitate was washed, dried, ignited, and calculated as the compound oxide and sesquioxide of manganese ($Mn_3 O_4$).

I. 2·1890 grm. of glass gave 0·0114 grm. of the above-named double oxide.

II. 2·1284 grm. of glass gave 0·0160 grm. of the double oxide.

*e.* DETERMINATION OF MAGNESIA.

The filtrate from the carbonate of manganese (*d*) was precipitated by phosphate of soda; the phosphate of magnesia and ammonia was washed, dried, ignited and weighed as pyrophosphate of magnesia.

I. 2·1890 grm. of glass gave 0·0177 grm. of pyrophosphate of magnesia.

II. 2·1284 grm. of glass gave 0·0177 grm. of pyrophosphate of magnesia.

*f.* DETERMINATION OF THE ALKALIES.

To determine the amount of the alkalies, a portion of the glass was fused with hydrate of baryta; the fused mass was digested in hydrochloric acid, evaporated to dryness and ignited, the residue again digested in hydrochloric acid, and then filtered from the insoluble silicic acid. Carbonate of ammonia was then added to the filtrate, to separate the alumina, sesquioxide of iron, baryta and lime; the solution filtered from the precipitate was evaporated to dryness and ignited, to drive off the ammoniacal salts, and the magnesia separated by means of baryta; the excess of baryta was separated by carbonate of ammonia, and filtered. The filtrate, evaporated to dryness and ignited, yielded the mixed chlorides of the alkaline metals; they were dissolved in water, bichloride of platinum added, and the solution evaporated to dryness on a water-bath; the residue was digested in strong alcohol, when the bichloride of platinum and potassium remained undissolved; it was collected on a weighed filter, washed with alcohol, and dried in a water-bath until it ceased to lose weight. The filtrate from the bichloride of platinum and potassium was evaporated to dryness, and after the addition of some oxalic acid to the residue, ignited till it was completely decomposed; the residue was digested in water, filtered, and the filtrate evaporated to dryness in a weighed capsule; its increase in weight gave the quantity of chloride of sodium.

1·5645 grm. of glass gave 0·9330 grm. of bichloride of platinum and potassium, and 0·0905 grm. of chloride of sodium.

From the results enumerated, the calculated per centage is as follows:

| | I. | II. | Mean. |
|---|---|---|---|
| Silicic acid | 72·84 | 73·42 | 73·13 |
| Lime | 10·75 | 10·11 | 10·43 |
| Alumina | 0·30 | — | 0·30 |
| Sesquioxide of iron | 0·13 | — | 0·13 |
| Magnesia | 0·21 | 0·30 | 0·26 |
| Protoxide of manganese | 0·37 | 0·54 | 0·46 |
| Soda | 3·07 | — | 3·07 |
| Potassa | 11·49 | — | 11·49 |
| | 99·16 | | 99·27 |

The amount of oxygen in the bases stands to the amount of oxygen in the silicic acid nearly as 1 : 6.

From the preceding analysis, it results that the composition of the glass for combustion-tubes does not differ very much from the material employed in goblets, as may be seen from the following comparison with the results of the chemists formerly named:—

| | Berthier. | Dumas. | Gras. | Peligot. |
|---|---|---|---|---|
| Silicic acid | 71·7 | 69·4 | 71·6 | 76 |
| Lime | 10.3 | 9·2 | 10·0 | 8 |
| Alumina | 0·4 | 9·6 | 2·2 | 1 |
| Sesquioxide of iron | 0·3 | — | 3·9 | — |
| Oxide of manganese | 0·2 | — | 0·2 | — |
| Magnesia | — | — | 2·3 | — |
| Soda | 2·5 | — | — | — |
| Potassa | 12·7 | 11·8 | 11·0 | 15 |
| | 98·1 | 100·0 | 101·2 | 100 |

In one of the last numbers of Dr. Otto's German translation of Professor Graham's Elements of Chemistry, recently published, I find the analysis of a combustion-tube enumerated, performed in the laboratory of Dr. Otto, which has not yet been published in the Journals. He obtained the following results:—

| | |
|---|---|
| Silicic acid | 74·0 |
| Lime | 7·2 |
| Alumina<br>Sesquioxide of iron | 0·1 |
| Potassa | 18·5 |
| | 100·0 |

The oxygen in the bases of this glass stands to the oxygen in the silicic acid likewise as 1 : 6. Soda is entirely absent, and completely replaced by potassa. The presence however of a small amount of soda does not seem to be injurious to the glass.

## VII.—*Analysis of an ancient Peruvian Alloy,*

By Henry How, Esq.

The yellow metallic plate which forms the subject of the following note was obtained for analysis from Sir James Clark by Dr. Hofmann. It had been taken from a band of similar plates found surrounding the skull of a skeleton (supposed to be that of an ancient Peruvian Chief or Inca) in the neighbourhood of Truxillo, in Peru.

A qualitative examination proved it to consist of gold, silver and copper.

The alloy was treated with nitric acid, and in this manner all the copper, and the greater part of the silver, were dissolved from the gold; the silver was thrown down by hydrochloric acid, and the copper precipitated from the filtrate by potassa, and weighed as black oxide. The residue left by nitric acid was treated by nitro-hydrochloric acid, the solution filtered from a little chloride of silver, and evaporated to dryness; the residue was ignited and weighed as gold, while the small portion of chloride of silver was added to the larger quantity obtained from the nitric solution.

I. 0·8722 grm. gave 0·3395 grm. of gold, 0·6340 grm. of chloride of silver, and 0·068 grm. of protoxide of copper.

II. 0·94 grm. gave 0·366 grm. of gold and 0·685 grm. of chloride of silver.

Numbers which lead to the following per centages:

| | I. | II. |
|---|---|---|
| Gold . . . . | 38·92 | 38·93 |
| Silver . . . | 54·72 | 54·82 |
| Copper . . . | 6·22 | — |
| | 99·86 | |

It cannot be known with certainty whether this plate consists of an artificial alloy, or is the crude product of a rough metallurgic working of an ore containing the three above-mentioned metals; the latter supposition is perhaps the more probable.

# RESEARCHES

IN

# ORGANIC CHEMISTRY.

## VIII.—*On Cochineal* (Coccus Cacti).

By Warren De la Rue, Esq., F.C.S. &c.

(Read before the Chemical Society of London.)

The beautiful theoretical results which have been lately obtained, by a closer examination of indigo blue and its products of decomposition, made it desirable to undertake similar investigations with other colouring matters. I made choice of the colouring principle of cochineal (*Coccus Cacti*), hoping that a detailed research might not only prove of interest in a scientific point of view, but also throw some light on its practical applications, and the more so, as the recent investigations of Preisser had seemed to point out a very close analogy in the chemical properties of a variety of colouring matters with indigo blue.

Before entering into the detail of my experiments, I think it desirable to give a brief outline of the results obtained by the chemists who have hitherto worked on this subject.

Dr. Jean Frédéric John* appears to have published the first analysis of cochineal: he does not describe his method, but merely states that it contains the following per centages:

| | |
|---|---|
| Colouring principle (semi-solid, soluble in water and alcohol) | 50·00 |
| Gelatine | 10·50 |
| Waxy fat | 10·00 |
| Modified mucus | 14·00 |
| Membrane | 14·00 |
| Alkaline phosphates and chlorides, phosphate of lime, phosphate of iron, and phosphate of ammonia | 1·50 |
| | 100.00 |

* Tableaux Chimiques du Règne Animal, quarto, translated from the German.

Pelletier* and Caventou, in a very long memoir read before the *Institut de France* in 1818, have gone very elaborately into the examination of cochineal, and obtained many interesting results. In analysing this substance, they employed the following process:— They removed the fatty bodies by boiling ether, in which they found the colouring matter but slightly soluble; these fatty substances, recovered by distilling off the ether, were considered to consist of stearine, oleine, and an aromatic acid, from which latter substance it was difficult to remove the adhering colouring matter.

The cochineal, exhausted with ether, was treated with alcohol of 40° Beaumé, which dissolved the colouring matter, together with a small quantity of fatty and nitrogenous substances.

On cooling, and by spontaneous evaporation, they obtained a granular red residue of a semi-crystalline appearance, and which they considered to be the colouring matter contaminated still with nitrogenous matter (*matière animalisée*) and some fatty bodies, the greater part of which remained undissolved in strong cold alcohol; by repeating the operation once or twice they considered that the substance was obtained almost in a state of purity. To remove the last traces of foreign matter, it was dissolved in strong alcohol, and an equal volume of ether added, *which precipitated the colouring matter and retained the fat,* which was still adhering to it. The colouring matter thus purified they named carmine (*carminium*), and described it as being very soluble in water, from which it did not crystallize, more or less soluble in alcohol, according to its strength, and quite insoluble in ether and the fixed and volatile oils. Acids did not precipitate it from its aqueous solution if free from animal matter. They found hydrochloric and sulphuric acid to decompose it; the latter with elimination of carbon. By the action of nitric acid they obtained an acid in prismatic crystals resembling oxalic acid, but differing in some of its properties.

On heating the "carmine" it intumesced and gave off carburetted hydrogen, a considerable quantity of oily substances, a little acid water, but no trace of ammonia. Chlorine and iodine decomposed it; the alkalies, in the commencement, produced merely a change in colour, turning it violet; but by the assistance of time or heat they effected a complete alteration. They found an aqueous solution of "carmine" to exhibit the following comportment with reagents.

Of the alkaline earths, lime only produced a precipitate; hydrate of alumina showed a marked affinity, absorbing the whole of the colouring matter from an aqueous as well as an alcoholic solution;

* Annales de Chimie et de Physique, sér. 2, tome VIII, p. 250. Journal de Pharmacie, sér. 2, tome IV, p. 193.

the presence of alum prevented this reaction: iron, copper, and silver salts were without reactions; terchloride of gold destroyed the colour; neutral salts of lead merely changed it to violet, except the neutral acetate, which precipitated it, the free acetic acid retaining a little of the compound in solution; the colouring matter could be recovered by decomposing the lead compound with hydrosulphuric acid. The nitrate of the suboxide of mercury gave a purple, and the nitrate of the protoxide a scarlet-red precipitate; the protochloride no precipitate; protochloride of tin gave a violet precipitate; the bichloride changed the colour to scarlet without causing a precipitate. Albumine and gelatine had no marked action; but if precipitated by reagents the colouring matter was carried down.

In a later communication (1832), Pelletier* gave the composition of the colouring matter as prepared by himself and Caventou. In a previous qualitative examination they had failed to exhibit the presence of nitrogen which M. Pelletier now detected. The substance was dried *in vacuo*, at a gentle heat, to remove every trace of alcohol and ether; burnt with oxide of copper it yielded:

| | |
|---|---|
| Carbon . . . . . | 49·33 |
| Hydrogen . . . . . | 6·66 |
| Nitrogen . . . . . | 3·56 |
| Oxygen . . . . . | 40·45 |
| | 100·00 |

M. Pelletier stated, however, that he did not greatly rely on the correctness of this analysis.

After alcohol had dissolved out all the colouring matter removable by it, they extracted the last traces, by repeatedly washing the residue with boiling water, and along with it a little fatty and some nitrogenous matter; the residue was a brownish transparent mass. The later decoctions, containing no red colouring matter, left likewise on evaporation a brownish transparent mass, which they considered identical with the organic residue of the insect. This animal matter had, according to them, some analogy with gelatine, but differed in many of its properties, as it did also from albumine and fibrine; they therefore considered it as peculiar to the cochineal insect; the alkalies and ammonia dissolved it readily; chlorine precipitated it; all acids and acid salts precipitated it, as also acetate of lead, salts of tin and copper, and nitrate of silver; and they considered the latter reagent as a good test of the purity of the colouring matter, as it did not

* Annales de Chimie et de Physique, sér. 2, tome LI, p. 194.

precipitate the latter if free from nitrogenous substances. If the colouring matter were contaminated with nitrogenous substances, all the salts which precipitated the latter carried down likewise some of the colouring matter.

An examination of the ashes showed the presence of phosphate of lime, carbonate of lime, chloride of potassium, and phosphate of potassa, to the extent of 0·7 per cent.

In the second part of the memoir, they went into the theory of the technical applications of the colouring matter: this having no reference to the present subject, I do not think it necessary to reproduce it here.

M. Lassaigne, in 1819,* examined Kermes (*Coccus ilicis*), an insect common in the South of Europe, and employed as a red dye before the discovery of America, and obtained by following the methods of Pelletier and Caventou, substances agreeing in their properties with the analogous ones found in cochineal.

M. F. Preisser†, in an elaborate paper on the origin and nature of colouring matters, has again drawn the attention of chemists to the subject. This gentleman, from a study of a variety of colouring substances, comes to the conclusion that all resemble indigo in its behaviour with reducing agents. He affirms, that he obtained by the action of hydrosulphuric acid on the lead compounds of a great number of organic colouring matters, substances bearing the same relation to the original colouring matters as white indigo does to blue indigo. In order to obtain the colourless modification of the colouring matter of cochineal, he adds what he terms "hydrate of oxide of lead" to an aqueous decoction of cochineal, the fats being previously removed by ether. The colouring matter is entirely removed by the so-called oxide of lead, which is nothing but a basic nitrate of lead, $2.(Pb\,NO_6, 2\,PbO) + 3\,HO$. The lead compound suspended in water (hot?) was decomposed by a stream of hydrosulphuric acid; the nearly colourless filtrate deposited, on cooling, needles of a pale yellow colour, which became perfectly white by washing with ether and pressing between bibulous paper; these crystals, which, according to his statement, are soluble in water and alcohol, but less so in ether, assume in contact with the atmosphere the purple-red of the colouring matter of cochineal. He moreover asserts, that his colourless modification gives a white lead salt on adding acetate of lead to its aqueous solution, and that this assumes a purple colour in contact with the air.

* Journal de Pharmacie, sér. 2, tome v, p. 435.

† Ibid, sér. 2, tome v, p. 191.

He proposes to give the name carmine, hitherto applied to the red colouring matter, to the white crystals, and to designate the red substance by the name "Carméine."

The statements of Preisser, generalizing most beautifully, under one head, the chemical character of all colouring matters, making indigo as it were the prototype of them all, could but induce other chemists to work out more in detail the relations cursorily pointed out in the memoir of this chemist. Unfortunately, a careful repetition of these experiments has not confirmed the basis on which his theory reposes.

M. A. E. Arppe repeated Preisser's experiments on the colouring matter of cochineal.* He found that, by proceeding in the manner described by Preisser, that he could only obtain a red solution, which on evaporation was converted into white crystals of oxalic acid by the nitric acid derived from the basic lead salt.

Arppe now prepared a pure oxide of lead by precipitating acetate of lead with potassa. He found that this would not take down the colouring matter in the cold, but by boiling it was carried down as a blue lake, which he decomposed by hydrosulphuric acid; the supernatant liquor was nearly colourless, the colouring matter he found adhered with great obstinacy to the sulphide of lead, from which water, alcohol and ammonia failed to separate it; but sulphide of ammonium and acids rendered it perceptible. He likewise tried to obtain the colouring matter in a state of purity by precipitating with hydrated oxide of lead an aqueous decoction of cochineal (previously purified from nitrogenous substances by nitrate of silver). On treating the precipitate by hydrosulphuric acid, he obtained a red liquor of *strongly acid reaction*, the acid of which could not have been derived from the oxide of lead: on evaporation, it left a dark red mass, emitting the smell of burnt sugar. Wishing to separate the acid, which he found contaminated the colouring matter, he prepared a strong aqueous decoction of cochineal, and after separating the nitrogenous matter by means of nitrate of silver, filtering, and then saturating by ammonia, and afterwards adding the hydrated oxide of lead, he found that the supernatant ammoniacal liquor, which was nearly colourless, *yielded by evaporation an acid liquid;* and on decomposing the lead lake with hydrosulphuric acid, he obtained a liquid slightly coloured (the colouring matter adhering to the sulphide of lead), *which was likewise acid.* From this he concluded that the colouring matter had not, up to that period, been obtained in a state of purity.

* Liebig's Annalen, vol. LV, p. 101.

### MICROSCOPIC EXAMINATION OF LIVING COCHINEAL.

By the kindness of Sir James Clark, who furnished me with specimens of the living insect, I have been enabled to study the physical characters of the colouring matter, as it exists in the organism of the insect before it is subjected to the process of drying for commerce. On examination by the microscope, the white dust which covers the insect and the adjacent parts of the cactus leaves, on which it feeds, has all the characters of an excrement; it has a curled cylindrical form, is of very uniform diameter, and of a white colour. On removing the powder with ether and piercing the side of the little creature, a quantity of a purplish red fluid exudes, which contains the colouring matter in minute granules assembled round a colourless and larger nucleus, these groups floating in a colourless fluid. It is therefore evident, that, whatever may be the function of the colouring matter, it has a distinct and marked form, and does not pervade, as a mere tint, the fluid portion of the insect.

### SEPARATION OF THE COLOURING MATTER.

It became evident, from a few preliminary experiments, that the investigation would be greatly facilitated by the employment of a large quantity of material; and as in the course of the inquiry different methods were adopted for the preparation of the colouring matter, capital letters will be used to designate the various preparations.

A. About 3 lbs. of ground cochineal (technically known as shelly black) was introduced into 15 gallons of boiling distilled water, and the mixture maintained at that temperature for twenty minutes; the decoction, strained through a sieve, was allowed to subside for a quarter of an hour and then decanted off; whilst still hot, the transparent liquid was mixed with basic nitrate of lead, added with caution to avoid excess; a fine purple lake was thus obtained, the supernatant liquor retaining only a pale buff tinge. After decantation of the supernatant liquor, the lake was thrown on a cloth filter and washed with distilled water until the filtrate gave but a slight opalescence with chloride of mercury, which was found to be a test for the presence of nitrogenous matter. The lead lake was then suspended in distilled water and treated with a copious stream of hydrosulphuric acid, when a precipitate of sulphide of lead and a deep red supernatant liquid was obtained; on stirring the liquid, this colour almost disappeared, the colouring matter being evidently

absorbed by the sulphide, agreeing perfectly with Arppe's observation. A fresh stream of gas reproduced the colour, which was again absorbed on stirring; after continuous treatment with hydrosulphuric acid, the lead lake being completely decomposed, the filtered liquid was evaporated in a water-bath to a syrupy consistence, and the evaporation finished as far as possible at a temperature of 38° C. The semi-solid substance thus obtained was of a deep purple colour, had a strongly acid reaction, and evolved the smell of burnt sugar, as noticed by Arppe. The weight of this substance, which I call crude carminic acid, was 3½ ozs., and 1 oz. more was obtained from the residue of cochineal by similar treatment.

B. On repeating the same process the whole product was lost. An excess of the basic nitrate having been employed, the nitric acid set free by the hydrosulphuric acid caused a violent decomposition, with evolution of nitrous fumes, as soon as the carminic acid arrived at a pasty consistence; this agrees also with Arppe's experience.

C. In this operation a decoction of cochineal, made in the described manner, was precipitated with a solution of acetate of lead acidulated with acetic acid (six parts by weight of crystallized acetate, and one part of strong acetic acid). The resulting lead lake, being very bulky, was washed by decantation with boiling distilled water, collected on a filter, dried in a current of warm air, and finely powdered; 17 ozs. of *crude carminate of lead* were thus obtained.

D. Half a pound of cochineal was boiled with five pints of alcohol, spec. grav. 0·830. The filtered tincture deposited on cooling a granular precipitate, consisting chiefly of fatty matter retaining a portion of colouring matter; on concentrating the tincture by distillation a further quantity was deposited, which was filtered off; the filtrate was evaporated to dryness *in vacuo*, when after eight weeks a gummy residue was obtained. This mass dissolved with great difficulty in a large quantity of absolute alcohol, a red flocculent substance, consisting chiefly of nitrogenous matter, remaining undissolved. The alcoholic solution filtered off from this deposit, concentrated by distillation and finally evaporated *in vacuo* over sulphuric acid, dried to a tenacious semi-solid mass, covered with a colourless oily fluid, and containing crystalline particles of a solid fat. After removal of the fats by means of ether, this mass was digested in water at 38° C., which partly dissolved it with a fine red colour, leaving a brown mass of resinous aspect behind, more of which deposited on the cooling of the coloured liquid; the decoction was

now evaporated to the consistence of a syrup, and finally dried *in vacuo* over sulphuric acid.

These are all the processes employed to *extract* the colouring matter from the cochineal; I may here remark, before entering on the details of its further purification, that I obtained other substances on evaporating the mother-liquors from which the colouring matter had been separated by lead salts, which will be hereafter described.

*Purification of the Carminic Acid.*—In my first attempts to purify the colouring matter I proceeded in the following way:—An aqueous solution of the crude carminic acid (A) was precipitated with acetate of lead, the precipitate of carminate of lead well-washed and decomposed by hydrosulphuric acid; the red supernatant liquid was first concentrated on the water-bath, and finally dried *in vacuo;* a highly hygroscopic purple residue was thus obtained.

I could not, by whatever means I adopted, effect the decolorization of the colouring principle. In several attempts I heated the solution for some hours to 100° C., keeping up a continuous current of hydrosulphuric acid, and in other experiments a stream was made to pass, for several days, through the disengaged colouring matter, but without the slightest change in its aspect. From these experiments, made with the greatest care and at several periods, I am led to the same conclusion as Arppe, that Preisser must have been mistaken in his results, and I regret that I cannot throw any light on the probable cause of his error.

Several combustions of the carminic acid, thus purified, were made; the resulting numbers however became useless by the subsequent observation that this acid was by no means pure. A sufficient quantity being incinerated, left a residue of acid reaction, which was suspected to contain phosphoric acid. Carminic acid burning only with great difficulty, it was reconverted into carminate of lead, the oxide of lead dissolved out of the residue, obtained after burning, by acetic acid, which left a white residue of metaphosphate of lead, together with a little lead. The white residue was soluble in dilute nitric acid, and exhibited, when treated before the blow-pipe, the characters of metaphosphate of lead; other tests likewise confirmed the presence of phosphoric acid. It will hereafter be seen that the process of extracting the colouring matter by alcohol (D) does not exclude the phosphoric acid, which in all probability existed in the colouring matter analysed by Pelletier. It is further evident, that the presence of phosphoric acid explains most satisfactorily the facts observed by Arppe.

*a.* In order to separate the phosphoric acid, another portion of crude carminic acid (A) was precipitated with acetate of lead. Three-fourths of the carminate of lead produced were decomposed by hydrosulphuric acid and evaporated to dryness in the way already mentioned. The dry mass being dissolved in cold absolute alcohol, and filtered from a slight flocculent brownish residue, was heated to ebullition in a water-bath and mixed with the remaining fourth of the carminate of lead, which had been previously reduced to a fine powder; the ebullition was continued for a few hours. In this manner the free phosphoric acid combined with the lead, liberating an equivalent proportion of carminic acid, which was taken up by the alcohol. The alcoholic solution was filtered whilst hot, concentrated by distillation, and then evaporated *in vacuo* in the presence of sulphuric acid; it dried into a granular mass of a deep purple-brown colour, detaching itself spontaneously from the sides of the vessel, and on examination by the microscope was found to be a beautiful transparent crimson substance, exhibiting only slight, if any, signs of crystalline structure; by pulverization it became of a fine scarlet colour; it left a mere trace of ash, and was found to be perfectly free from phosphoric acid. It was highly hygrometric.*

Burnt with chromate of lead:

I. 0·4647 grm. of substance gave:
0·9096 „ of carbonic acid, and
0·2175 „ of water.

II. 0·4630 „ of substance gave:
0·9105 „ of carbonic acid, and
0·2140 „ of water.

For the latter analysis I am indebted to my friend Mr. Nicholson.

*b.* A second preparation of carminic acid was made by operating on the crude carminate of lead (C) and treating the resulting crude carminic acid in the manner just described for the preparation *a.* It left on incineration 0·2 per cent. of ash (0·1609 grm. giving 0·0003 grm. ash), which was neglected in the following analyses:

III. 0·3710 grm. of substance gave:
0·7316 „ of carbonic acid, and
0·1710 „ of water.

* In consequence of this, it was found convenient to dry the carminic acid intended for analysis in little stoppered tubes in the air-pump, as the stopper could be rapidly inserted after desiccation, and access of air effectually prevented.

IV. 0·3685 „ of substance gave:
0·7235 „ of carbonic acid, and
0·1722 „ of water.

*c.* To effect the purification of the carminic acid (D) obtained by digesting cochineal in alcohol, it was dissolved in water and precipitated by acetate of lead; the filtrate was found to contain nitrogenous matter, and the carminate of lead to be contaminated with phosphate of lead; it was therefore treated in the manner already detailed.

V. 0·3925 grm. of this substance gave:
0·7658 „ of carbonic acid, and
0·1780 „ of water.

*d.* A fourth preparation of carminic acid was obtained by substituting phosphoric acid for hydrosulphuric in the decomposition of the crude carminate of lead (C), and evaporating the carminic acid to dryness in contact with a fresh portion of carminate of lead; this did not however separate entirely the phosphoric acid, it was therefore redissolved in boiling absolute alcohol, and maintained some time at that temperature with more carminate of lead. On analysis:

VI. 0·3805 grm. of substance gave:
0·7530 „ of carbonic acid, and
0·1848 „ of water.

Pelletier having obtained in his analysis of "carmine" (carminic acid) as much as 8·56 per cent. of nitrogen, all the before-cited preparations of carminic acid were carefully examined qualitatively for nitrogen by heating with soda-lime, and without exception gave indications of its presence; in most cases but a mere trace was found, but I thought it necessaary notwithstanding to make a few quantitative determinations, especially as M. Berzelius* had pointed out the improbability of it being an essential constituent.

The last preparation (*d*) appearing to contain more than any of the others, it was chosen and burnt with soda-lime.

It was indispensable in experiments of this nature to test the purity of the soda-lime as regarded the absence of ammonia. A tube having 9 inches of its length filled with soda-lime was heated to redness, just as in a nitrogen determination; the hydrochloric acid, being treated with bichloride of platinum in the usual manner, gave 7·5 milligrammes of bichloride of platinum and ammonium; a repe-

* Traité de Chim. tome III, p. 808. Brussels, edit. 1839.

tition of the experiment gave a similar result. This allowance has not been made on all the nitrogen determinations by soda-lime.

0·5938 grm. of carminic acid (*d*) gave:

0·0717 „ of bichloride of platinum and ammonium = 0·76 per cent of nitrogen.

This quantity of nitrogen could not be supposed to belong to the composition of the colouring matter, but was evidently due to some foreign substance, and not improbably to ammonia. In order to purify the carminic acid still more, the same specimen (*d*) was dissolved in a small quantity of boiling absolute alcohol, and the filtered solution mixed with three times its bulk of anhydrous ether; a splendid scarlet precipitate was immediately produced, which absorbed water rapidly from the atmosphere, and agglutinated into a dark purple mass; when dried it weighed 0·3 grm. (*e*). The filtrate, which was of a pale orange-red colour, left, on evaporation, 0·5 grm. of carminic acid (*f*).

0·2635 grm. (*e*) burnt with soda-lime, gave:

0·0637 „ of bichloride of platinum and ammonium = 1·52 per cent. of nitrogen.

0·4732 grm. (*f*) gave:

0·0150 „ of bichloride of platinum and ammonium = 0·2 per cent. of nitrogen.

We have therefore (*e*) 0·3 grm. found to contain by analysis 1·5 per cent. of nitrogen, and (*f*) 0·5 grm. 0·2 per cent., $\frac{(3\times 1{\cdot}5 + (5\times 0{\cdot}2)}{8}$ = 0·69 average per cent., which agrees closely with 0·76, found previous to treatment with ether.

*g*. Another preparation of carminic acid was obtained by precipitating crude carminic acid with acidulated acetate of copper, which salt was found to carry down the carminic acid, and to leave in solution by far the greater portion of the phosphoric acid. The carminate of copper, which occupied a long time in washing, was collected and decomposed by hydrosulphuric acid. The filtrate was evaporated to dryness, dissolved in boiling absolute alcohol, filtered, concentrated by distillation, and again evaporated to dryness *in vacuo*. It still contained a trace of phosphoric acid. On evaporating the mother-liquor and filtering, from an impure carminate of copper which deposited as the acetic acid was driven off, and again concentrating to dryness, a brown mass was obtained, which on incineration left a greenish-white very hygrometric ash, in which phosphoric acid, soda and copper were found. Burnt with chromate of lead:

VII. 0·4020 grm. of carminic acid (*g*) gave:
0·7842 „ of carbonic acid, and
0·1662 „ of water.

This acid, however, still retained some impurities: on incineration it left 0·4 per cent. of ash (0·5489 grm. giving 0·0022 grm. ash), and examined for nitrogen it gave the following numbers:

0.4731 grm. burnt with soda-lime gave:
0·0150 „ of bichloride of platinum and ammonium = 0·2 per cent. of nitrogen.

*h*. In order to separate these impurities, the greater portion was dissolved in boiling absolute alcohol, and filtered from a slight residue; the remainder, about an eighth, was converted into carminate of lead, digested with the boiling alcoholic solution for some hours, the alcoholic tincture filtered off whilst hot and mixed with about six times its volume of anhydrous ether; this threw down a bulky precipitate of a fine red colour, which was separated by filtration, and the filtrate concentrated in a retort, and finally evaporated to dryness *in vacuo* (*h*).

*i*. The precipitate retained on the filter was dried *in vacuo*, then dissolved in as small a quantity of alcohol as possible, and again mixed with a large quantity of ether; this determined a precipitate which was no longer of a fine red, but of a brown colour, and on re-solution and similar treatment, it diminished in quantity and became darker in colour, leaving the colouring matter in solution. From the filtrates a quantity of carminic acid (*i*) was obtained on evaporating to dryness *in vacuo*. It, therefore, appears that the ether precipitates a nitrogenous body which carries down with it variable quantities of carminic acid, according as a larger or smaller relative proportion is present. The carminic acid (*h*) was found to be free from phosphoric acid as well as nitrogen.

0·3003 grm. burnt with soda-lime gave:
0·0015 „ bichloride of platinum and ammonium = 0·03 per cent. of nitrogen.

From this analysis, I venture to assert that the colouring principle of cochineal contains no nitrogen, thus fully confirming the anticipation of Berzelius. We can now understand from the preparation of the specimen of carminic acid (*e*), that the method employed by Pelletier for the preparation of the substance he analysed was calculated to accumulate all the nitrogenous matter contained originally in his alcoholic decoction; a fact which fully explains the large amount of nitrogen he obtained in his analysis.

An analysis of the carminic (*h*) acid by chromate of lead gave the following results:

VIII. 0·3167 grm. of substance gave:
0·6203 „ of carbonic acid, and
0·1402 „ of water.

The following table exhibits the per centage results deduced from the foregoing analyses: the specimens were all dried over sulphuric acid *in vacuo*, with the exception of analysis VII., in which the carminic acid was dried at 100° C.

| | I. | II. | III. | IV. | V. | VI. | VII. | VIII. | Mean. |
|---|---|---|---|---|---|---|---|---|---|
| Carbon . . | 53·38 | 53·63 | 53·78 | 53·55 | 53·21 | 53·97 | 53·20 | 53·42 | 53·51 |
| Hydrogen . | 5·20 | 5·14 | 5·12 | 5·19 | 5·04 | 5·39 | 4·59 | 4·92 | 5·07 |

By the analysis of a copper salt of carminic acid hereafter to be mentioned, it became probable that carminic acid might still retain, when only dried *in vacuo*, a portion of the solvents employed; a presumption which was supported by the analysis VII., in which the substance analysed had been dried at 100° C., and which gave a smaller per centage of hydrogen. A portion of carminic acid (*i*), being first dried *in vacuo*, and then heated to a temperature of 121° C., was found to yield a small quantity of acetic acid, and was not altered in its properties, which were not in fact changed even at a temperature of 136° C.

In the following analyses, the carminic acid, previously dried *in vacuo*,* and then at a temperature of 120° C., gave, on burning with chromate of lead, the following results:—

IX. 0·3347 grm. of the acid (*h*) gave:
0·6648 „ of carbonic acid, and
0·1381 „ of water.
X. 0·3583 „ of the acid (*i*) gave:
0·7108 „ of carbonic acid, and
0·1504 „ of water.

These analyses give the following per centage quantities:—

| | IX. | X. |
|---|---|---|
| Carbon . . . . | 54·17 | 54·10 |
| Hydrogen . . . | 4·58 | 4·65 |

The analysis IX. being of the same preparation as had served for analysis VIII., it is fair to presume that all the other specimens of carminic acid would have given the same per centage quantities as

* The carminic acid fuses if exposed to a temperature of 120° C. without having been previously dried *in vacuo*.

the specimen (*h*) if dried at 120° C., as this particular specimen, dried *in vacuo*, yielded numbers in close accordance with the mean of the other analyses.

These numbers converted into the most simple expression lead to the following formula,

$$C_{14}\,H_7\,O_8;$$

but an analysis of a copper salt renders it probable that this formula has to be doubled, and that the composition of carminic acid is expressed by the formula,

$$C_{28}\,H_{14}\,O_{16},$$

as may be seen from the following table containing the comparison of the theoretical per centages with the mean of analyses IX. and X.

| | Theory. | | Experiment. |
|---|---|---|---|
| 28 equivs. of Carbon . . . . . | 168 | 54·19 | 54·18 |
| 14 „ of Hydrogen . . . . . | 14 | 4·52 | 4·62 |
| 16 „ of Oxygen . . . . . | 128 | 41·29 | — |
| 1 equiv. of Carminic acid . . . . | 310 | 100·00 | |

From the foregoing experiments, it seems that the best method of obtaining pure carminic acid is to precipitate the aqueous decoction by acetate of lead; to decompose the washed carminate of lead by hydrosulphuric acid, and to throw down the carminic acid once more by acetate of lead, previously mixed with acetic acid; to decompose the carminate of lead by hydrosulphuric acid; to evaporate to dryness and redissolve the carminic acid in absolute alcohol; then to digest the alcoholic tincture with carminate of lead; and lastly, to precipitate the trace of nitrogenous matter by ether, the pure carminic acid is obtained from the filtrate.

As thus prepared, carminic acid has the following properties. It is a purple-brown friable mass, transparent and red when viewed by the microscope, and pulverizable to a fine red powder; soluble in water and alcohol in all proportions, very slightly soluble in ether, which does not, however, precipitate it from its alcoholic solution if free from nitrogenous matter. It is soluble without decomposition in concentrated hydrochloric and sulphuric acids. It is decomposed by chlorine, iodine and bromine, which change its colour to yellow, and the latter on warming, or by standing, gives a yellow precipitate

soluble in alcohol. Nitric acid decomposes it even if highly diluted: I shall have occasion to refer to this decomposition presently. It bears a temperature of 136° C. without decomposition; on gradually increasing the temperature a quantity of an acid liquor is produced, and at a red heat it intumesces and gives off a small quantity of red fumes, which condense: it gives no trace of oily matter.

The aqueous solution has a feeble acid reaction; it does not absorb oxygen. A volume of this gas contained in a tube with carminic acid over mercury did not change by absorption after exposure for several months. The fixed alkalies and ammonia give no precipitate in the aqueous solution, merely changing its colour to purple; in the alcoholic tincture they produce purple precipitates; all the alkaline earths produce purple precipitates; sulphate of alumina gives no precipitate, but on addition of a drop of ammonia the carminic acid is immediately taken down as a beautiful crimson lake; acetates of lead, copper, zinc and silver give purple precipitates, the latter is immediately decomposed, and silver deposited; the nitrates of lead, mercury and silver reddish precipitates; protochloride and bichloride of tin give no precipitates, but change the colour to a deep crimson.

The acid character of carminic acid being so very little pronounced, I met with considerable difficulties in determining its atomic weight; it is only with great reserve that I bring forward the formula before cited. Several attempts were made to produce soda, baryta, lead and copper compounds, but it was only with the copper salt that I obtained results agreeing in different preparations.

It seems that carminic acid attaches itself to salts, for it was found that the precipitants could be removed from the precipitates only with the greatest difficulty. I omit several soda, baryta and lead determinations which have not led to any satisfactory result, and confine myself to the statement of the result of the analysis of the copper compound. It was obtained by acidulating an aqueous solution of pure carminic acid with acetic acid, and then precipitating by the cautious addition of acetate of copper, so as to leave an excess of carminic acid in the liquid. The precipitate was well-washed by decantation (by which a great loss was sustained) and dried. It formed into masses of a bronze colour, very hard and difficult to powder. Two specimens were prepared at different times (*a* and *b*).

I. 0·2800 grm. (*a*) dried at 100° C. left, after ignition and treatment with nitric acid and re-ignition,
0·0330 „ of protoxide of copper.

II. 0·3782 grm. (*b*) dried at 100° C. gave:
0·0426 „ of protoxide of copper.

III. 0·4702 grm. (*b*) dried at 100° C. gave on burning with chromate of lead:
0·8210 „ of carbonic acid, and
0·1743 „ of water.

These numbers lead to the following per centage results:—

| | I. | II. | III. |
|---|---|---|---|
| Protoxide of Copper . | 11·78 | 11·27 | — |
| Carbon . . . . . | — | — | 47·62 |
| Hydrogen . . . . | — | — | 4·12 |

agreeing closely with the formula,

$$CuO, C_{28} H_{14} O_{16},$$

as will be seen from a comparison of the theoretical and experimental numbers.

| | | Theory. | | Experiment. |
|---|---|---|---|---|
| 1 equiv. | of Protoxide of Copper . | 39·6 | 11·33 | 11·52 |
| 28 „ | of Carbon . . . . . | 168·0 | 48·05 | 47·62 |
| 14 „ | of Hydrogen . . . . | 14·0 | 4·01 | 4·12 |
| 16 „ | of Oxygen . . . . . | 128·0 | 36·61 | — |
| 1 equiv. of the Copper compound . | | 349·6 | 100·00 | |

### ACTION OF NITRIC ACID ON CARMINIC ACID.

*Nitrococcusic Acid.*—When acting with nitric acid on "carmine" (carminic acid), MM. Pelletier and Caventou obtained white acid crystals resembling oxalic acid, but differing from this acid in several of its properties. M. Arppe found that the acid produced was oxalic acid. In my experiments I obtained the following results:—One pound and a half of crude carminic acid was gradually introduced into ten pounds of nitric acid, spec. grav. 1·4, and digested at a moderate heat; a violent evolution of nitrous fumes succeeded each addition of the carminic acid; after the whole quantity had been introduced, and the action had somewhat subsided, the mixture was transferred into a smaller vessel, and the action continued at the boiling-point for about two hours; by this time the greater part of the nitric acid had evaporated, and on withdrawing the vessel from the fire and allowing the mixture to cool, a crystalline cake was obtained, which on examination was found to consist partly of a new acid and partly of oxalic acid. To separate the oxalic acid, it was dissolved in a large quantity of boiling water and treated with nitrate

of lead as long as any precipitate of oxalate of lead formed; this was collected and decomposed by boiling with dilute sulphuric acid; the filtrate from the sulphate of lead yielded a large quantity of prismatic crystals of oxalic acid, which were obtained perfectly white and pure after two or three crystallizations with the aid of a little animal charcoal.

The yellow liquid filtered from the oxalate of lead was concentrated and separated from a fresh portion of oxalate which deposited on concentration, the evaporation was then continued until a large quantity of crystals formed; the solution on cooling deposited a very bulky mass of yellow rhombic prisms, which were drained and dried, and re-dissolved in a sufficient quantity of boiling water, which on cooling deposited the acid (for which I propose the name of nitrococcusic acid) in beautiful crystals free from any lead salt; it was recrystallized twice more, by which means it was obtained perfectly pure.

Several preparations were made, sometimes using pure carminic acid, at other times carminate of lead, with similar results.

The analyses of four different preparations dried at 100° C. gave, on burning with chromate of lead (unless otherwise stated), the following numbers:

I. 0·3152 grm. (*a*) gave:
0·3892 „ of carbonic acid, and
0·0561 „ of water.
II. 0·2500 „ (*a*) gave:
0·3080 „ of carbonic acid, and
0·0445 „ of water.

(For this analysis I am indebted to Mr. Nicholson.)

III. 0·3068 grm. (*a*) gave:
0·3820 „ of carbonic acid, and
0·0502 „ of water.
IV. 0·4498 „ (*b*) gave:
0·5626 „ of carbonic acid, and
0·0757 „ of water.
V. 0·4461 „ (*c*) gave:
0·5515 „ of carbonic acid, and
0·0777 „ of water.
VI. 0·4503 „ (*d*) burnt with oxide of copper, gave:
0·5585 „ of carbonic acid, and
0·0757 „ of water.

VII. 0·4796 grm. (*c*) gave, on being burnt with oxide of copper, a layer of copper 12 inches long being used so as to completely decompose the binoxide of nitrogen,
0·5882 „ of carbonic acid, and
0·0815 „ of water.

The foregoing analyses lead to the following per centage quantities:

| | I. | II. | III. | IV. | V. | VI. | VII. |
|---|---|---|---|---|---|---|---|
| Carbon . . | 33·67 | 33·60 | 33·95 | 34·11 | 33·72 | 33·82 | 33·44 |
| Hydrogen . | 1·98 | 1·98 | 1·82 | 1·87 | 1·93 | 1·87 | 1·89 |

In the following experiments the nitrogen of the nitrococcusic acid was ascertained by burning with oxide of copper in an atmosphere of carbonic acid.

VIII. 0·6808 grm. (*b*) dried at 100° C. gave 84 cubic centimetres of moist nitrogen at 6°·5 C. and 0·7585 m. barometer corrected.

IX. 0·7162 grm. (*c*) dried a 100° C. gave 91·5 cub. cent. of moist nitrogen at 17°·5 C. and 0·7641 m. barometer corrected.

These numbers correspond to the following per centage quantities:

| | VIII. | IX. | Mean. |
|---|---|---|---|
| Nitrogen . . | 15·03 | 14·92 | 14·97 |

X. In this experiment the nitrogen was determined according to Bunsen's* method, which consists in burning the substance mixed with oxide of copper, in the presence of copper-turnings in a hard glass tube. The tube having been freed from air by a stream of hydrogen, is then exhausted, sealed hermetically, and placed in an iron mould filled with plaster of Paris; it is then heated to redness and allowed to cool. After the combustion, the gas is transferred into a graduated jar over mercury and its volume noted; the carbonic acid being absorbed by a potassa ball, the volume is again read off. This analysis gave the following numbers:

| | Vol. | Temp. | Diff. of level. | Barom. |
|---|---|---|---|---|
| Carbonic acid + nitrogen (moist) | 123 | 20°·7 C. | 0$^{m}$·0640 | 0$^{m}$·7543 |
| Nitrogen . . . . . | 22·2 | 20°·0 | 0$^{m}$·1650 | 0$^{m}$·7529 |

The height of the column of mercury in the eudiometer above the level in the trough and the barometric column are corrected for temperature.

| | | | | | |
|---|---|---|---|---|---|
| Carbonic acid + nitrogen corrected to | 0° C. | and barom. | | | 1$^{m}$ = 76·84 |
| Nitrogen .. .. | „ | „ | 0° | „ | „ 1$^{m}$ = 12·16 |
| Carbonic acid .. .. | „ | „ | 0° | „ | „ 1$^{m}$ = 64·68 |

* Liebig's Annalen, vol. xxxvii, p. 27.

Hence we arrive at $\frac{64{\cdot}68}{12{\cdot}16} = 5{\cdot}32$, which is the ratio of carbon equivalents to one nitrogen equivalent.

The preceding analyses of nitrococcusic acid agree with the following formula,

$$C_{16}\,H_5\,N_3\,O_{18},$$

confirmed by the analyses of several of its compounds, as will be seen on referring to the table.

| | Theory. | | Experiment. Mean. |
|---|---|---|---|
| 16 equivs. of Carbon . . . . | 96 | 33·45 | 33·75 |
| 5 „ of Hydrogen . . . . | 5 | 1·74 | 1·91 |
| 3 „ of Nitrogen . . . . | 42 | 14·63 | 14·97 |
| 18 „ of Oxygen . . . . | 144 | 50·18 | — |
| 1 equiv. of Nitrococcusic acid . | 287 | 100·00 | |

By analysis VII., in which the precaution was taken of using a very long layer of copper turnings, there was obtained, carbon 33·44, hydrogen 1·89; these numbers agree as closely as possible with the theoretical quantities, as does likewise the nitrogen determination (X.) by Bunsen's method; in this experiment the ratio of carbon equivalents to nitrogen equivalents was found to be as 5·32 to 1, or as 16 equivs. of carbon to 3·007 equivs. of nitrogen; taking analysis VII. as the basis of calculation, it gives 14·67 per cent. of nitrogen, the theoretical number being 14·63.

The acid, as it separates from its aqueous solution, contains water of crystallization, which it loses at 100° C.; four experiments gave the following results:—

| | | | | |
|---|---|---|---|---|
| 0·4800 grm. | lost 0·0289 grm. | = 6·02 | per cent. |
| 0·6613 „ | „ 0·0395 „ | = 5·97 | „ |
| 0·6586 „ | „ 0·0385 „ | = 5·84 | „ |
| 0·4804 „ | „ 0·0289 „ | = 6·01 | „ |
| | Mean . . | = 5·96 | „ |

This mean corresponds perfectly with the formula

$$C_{16}\,H_5\,N_3\,O_{18} + 2Aq,$$

as may be seen by a comparison of the theoretical and experimental numbers.

| | Theory. | | Experiment. Mean. |
|---|---|---|---|
| 1 equiv. of Acid . . . . . | 287 | 94·10 | 94·04 |
| 2 equivs. of Water . . . . . | 18 | 5·90 | 5·96 |
| 1 equiv. crystallized Nitrococcusic acid | 305 | 100·00 | 100·00 |

*Properties of Nitrococcusic Acid.*—It is of a yellow colour, crystallizing in rhombic plates, and presenting very different aspects according to the circumstances under which it is crystallized. Its solution stains the skin yellow, it is soluble in cold, but considerably more so in hot water; soluble in alcohol, and very soluble in ether. All its salts dissolve readily in water, and most of them in alcohol; it deflagrates violently on being heated; it dissolves iron and zinc, becoming dark-coloured. It is decomposed by sulphide of ammonium with separation of sulphur, and the formation of the ammonium salt of a new acid, which I have not yet examined.

### COMPOUNDS OF NITROCOCCUSIC ACID.

*Nitrococcusate of Potassium.*—I have prepared this salt by two different methods.

*a.* A solution of nitrococcusic acid in boiling water was accurately saturated with carbonate of potassa; by evaporation to a small bulk and cooling, the salt was obtained in small yellow crystals; it was purified by draining and recrystallizing.

*b.* An etherial solution of the acid was precipitated by the cautious addition of an alcoholic solution of potassa; the pale yellow precipitate washed with ether and dried, then dissolved in as small a quantity of cold water as possible, and the solution poured into about five times its bulk of absolute alcohol; after standing some time the salt crystallized in well-formed crystals; it was washed with ether and dried. The etherial washings being added to the mother-liquor, a further portion was obtained and washed with ether. The latter process is less troublesome than the process *a*.

I. 0·5469 grm. (*a*) dried at 100° C. was dissolved in a small quantity of boiling water and decomposed by sulphuric acid; dried in a water-bath, the nitrococcusic acid, removed by ether and the residue ignited, gave:
0·2606 „ of sulphate of potassa.
II. 0·4383 „ „ (*b*) dried at 132° C. gave:
0·2103 „ „ sulphate of potassa.
III. 0·6251 „ „ (*b*) dried at 100° C. and burnt with chromate of lead, gave:
0·6064 „ „ carbonic acid, and
0·0662 „ „ water.

These numbers give the following per centage quantities:

| | I. | II. | III. |
|---|---|---|---|
| Potassium . | 21·36 | 21·51 | — |
| Carbon . . | — | — | 26·46 |
| Hydrogen . . | — | — | 1·18 |

corresponding with the formula

$$2\,K, C_{16}\,H_3\,N_3\,O_{18}$$

as may be seen by comparing the theoretical and experimental numbers.

| | Theory. | | Experiment. Mean. |
|---|---|---|---|
| 2 equivs. of Potassium . | 78 | 21·49 | 21·44 |
| 16 „ of Carbon . . | 96 | 26·45 | 26·46 |
| 3 „ of Hydrogen . | 3 | 0·83 | 1·18 |
| 3 „ of Nitrogen . . | 42 | 11·57 | — |
| 18 „ of Oxygen . . | 144 | 39·66 | — |
| 1 equiv. of Nitrococcusate of Potassium . | 363 | 100·00 | |

I was not successful in preparing a nitrococcusate of potassium with one equivalent of fixed base; the method I adopted was saturating a given weight of acid with carbonate of potassa, and then adding the same amount of acid to the bibasic potassium salt; on washing with ether the greater part of the excess of acid was removed, leaving the bibasic salt behind.

*Nitrococcusate of Ammonium.*—This salt was prepared by passing an excess of dry ammoniacal gas through an etherial solution of the acid dried in the atmosphere; the solution became turbid, and by standing for a short time deposited the salt in clusters of needles adhering firmly to the sides of the vessel; these were removed, washed with ether, and dried on bibulous paper. It is volatile, and sublimes on being heated, most probably with decomposition.

I. 0·6011 grm. of the salt dried *in vacuo* was dissolved in a small quantity of boiling water and decomposed by strong hydrochloric acid, which immediately separated the acid in crystals; the mixture was dried in a water-bath, and the nitrococcusic acid removed by ether, a little bichloride of platinum and alcohol being added to the etherial washings to precipitate a trace of chloride of ammonium. The residue, precipitated as bichloride of platinum and ammonium, gave:

0·8208 grm. of the double chloride.

II. 0·6126 „ dried *in vacuo* and burnt with oxide of copper, the mixture being made in the combustion-tube, gave

0·6525 „ of carbonic acid, and

0·2191 „ of water.

These numbers correspond with the following per centage quantities:

| | I. | II. |
|---|---|---|
| Ammonium . . . . | 11·01 | — |
| Carbon . . . . . | — | 29·05 |
| Hydrogen . . . . | — | 3·97 |

agreeing closely with the following formula,

$$2NH_4, C_{16} H_3 N_3 O_{18} + HO,$$

as may be seen by a comparison of the theoretical and experimental numbers.

| | Theory. | | Experiment. |
|---|---|---|---|
| 16 equivs. of Carbon . . . . . | 96 | 29·09 | 29·05 |
| 12 „ „ Hydrogen . . . . . | 12 | 3·64 | 3·97 |
| 5 „ „ Nitrogen . . . . . | 70 | 21·21 | — |
| 19 „ „ Oxygen . . . . . | 152 | 46·06 | — |
| 1 eq. of Nitrococcusate of Ammonium | 330 | 100·00 | |

| | Theory. | | Experiment. |
|---|---|---|---|
| 2 equivs. of Ammonium . . . . | 36 | 10·91 | 11·01 |
| 1 equiv. of Acid . . . . . | 285 | 68·37 | — |
| 1 „ of Water . . . . . | 9 | 2·72 | — |
| 1 eq. of Nitrococcusate of Ammonium | 330 | 100·00 | |

*Nitrococcusate of Barium* was prepared by adding an excess of a solution of baryta to an aqueous solution of nitrococcusic acid, a stream of carbonic acid gas being passed through the solution to separate the excess of baryta. The solution was warmed, filtered and evaporated in a water-bath, and again filtered from a small quantity of carbonate of baryta. The evaporation being continued until a pellicle formed on the surface, the solution on cooling deposited this salt in minute yellow crystals. It is insoluble in alcohol, which precipitates it in the form of a jelly from the aqueous solution.

I. 0·6750 grm. of substance dried at 100° C. and decomposed by sulphuric acid, gave:
0·3602 „ of sulphate of barium.

II. 0·6439 „ of nitrococcusate of barium dried at 100° C. and burnt with chromate of lead, gave:
0·5185 „ of carbonic acid, and
0·0800 „ of water.

These numbers correspond to the following per centage quantities:

| | I. | II. |
|---|---|---|
| Barium . . . . . | 31·40 | — |
| Carbon . . . . . | — | 21·96 |
| Hydrogen . . . . | — | 1·38 |

agreeing with the formula,

$$2\,Ba, C_{16}\,H_3\,N_3\,O_{18} + 2HO,$$

as may be seen from the following table:

| | | Theory. | | Experiment. |
|---|---|---|---|---|
| 2 equivs. | of Barium . . . . | 137·28 | 31·18 | 31·40 |
| 16 „ | of Carbon . . . . . | 96·00 | 21·80 | 21·96 |
| 5 „ | of Hydrogen . . . . | 5·00 | 1·14 | 1·38 |
| 3 „ | of Nitrogen . . . . | 42·00 | 9·54 | — |
| 20 „ | of Oxygen . . . . | 160·00 | 36·34 | — |
| 1 eq. | of Nitrococcusate of Barium | 440·28 | 100·00 | |

*Nitrococcusate of Silver.*—I attempted to make this salt by boiling oxide of silver with an aqueous solution of nitrococcusic acid, but this effected evidently a decomposition of the acid, a large quantity of carbonic acid being evolved; after warming the filtered liquor, a brown deposit was formed. On filtering off this brown deposit, a silver salt was obtained by evaporation, which yielded on analysis—

| | |
|---|---|
| Silver . . . . . | 35·47 |
| Carbon . . . . . | 23·64 |
| Hydrogen . . . . | 1·26 |

per centage numbers not reconcilable with those of nitrococcusate of silver.

On decomposing a hot solution of this salt with hydrochloric acid a new acid was obtained, perfectly distinct from nitrococcusic acid; it crystallized in long needles; very insoluble in water, but soluble in ether and alcohol. I refrain from giving any further account of this acid until the study is completed.

In order to avoid decomposition, the nitrococcusate of silver was prepared without the aid of heat, by dissolving carbonate of silver in a cold aqueous solution of nitrococcusic acid, and evaporating the filtered solution *in vacuo* over sulphuric acid. The salt crystallized in long bulky needle-like crystals of a yellow colour; when dried at 100° C. the powdered salt becomes deep orange.

It is soluble in alcohol and water, and is highly explosive when

heated; in small quantities it may be decomposed by a progressive heat without any violent action; but on attempting to decompose a quantity amounting to 0·45 grm. in a porcelain crucible, heated in an air-bath, the salt exploded with great violence, shattering the copper air-bath, and driving fragments of the crucible through the copper; the temperature was noted just before the explosion, the thermometer standing at 200° C.; the silver was, therefore, determined as chloride.

I. 0·4698 grm. of substance (*a*) dried at 100° C. and decomposed by nitric acid, and the silver precipitated by the addition of hydrochloric acid, gave:
0·2675 „ chloride of silver.
II. 0·5085 „ of substance (*b*) dried at 100° C. gave:
0·2892 „ chloride of silver.
III. 0·8184 „ of substance (*a*) dried at 100° C. and burnt with oxide of copper, gave:
0·5700 „ carbonic acid, and
0·0554 „ water.

Corresponding to the following per centage quantities:

| | | | |
|---|---|---|---|
| Silver . . . . . | 42·85 | 42·80 | — |
| Carbon . . . . | — | — | 18·99 |
| Hydrogen . . . | — | — | 0·75 |

and agreeing closely with the following formula,

$$2\,Ag, C_{16}H_3N_3O_{18},$$

as may be seen by the following table:—

| | | Theory. | | Experiment Mean. |
|---|---|---|---|---|
| 2 equivs. | of Silver . . . . . | 216 | 43·114 | 42·82 |
| 16 „ | of Carbon . . . . . | 96 | 19·162 | 18·99 |
| 3 „ | of Hydrogen . . . . | 3 | 0·599 | 0·75 |
| 3 „ | of Nitrogen . . . . | 42 | 8·383 | — |
| 18 „ | of Oxygen . . . . . | 144 | 28·742 | — |
| 1 equiv. | of Nitrococcusate of Silver | 501 | 100·000 | |

*Nitrococcusate of Copper.*—This was made by dissolving carbonate of copper in nitrococcusic acid and deposited on evaporation in pale apple-green needles. I made no analysis of this salt.

The following is a synoptical table of the analyses of nitrococcusic acid and its compounds:—

Hydride of nitrococcusic acid . . . . $2H, C_{16} H_3 N_3 O_{18}$.
Hydride of nitrococcusic acid as crystallized from water . . . . . $2H, C_{16} H_3 N_3 O_{18} + 2$ Aq.
Nitrococcusate of potassium . . . . $2K, C_{16} H_3 N_3 O_{18}$.
Nitrococcusate of ammonium . . . $2NH_4, C_{16} H_3 N_3 O_{18} +$ Aq.
Nitrococcusate of barium . . . . . $2Ba, C_{16} H_3 N_3 O_{18} + 2$ Aq.
Nitrococcusate of silver . . . . . $2Ag, C_{16} H_3 N_3 O_{18}$.

The properties of nitrococcusic acid, and its salts, exhibit a great analogy with those of a number of acids obtained by the action of nitric acid on organic bodies, more especially nitropicric and styphnic acids, from which it differs by the greater solubility of its salts.

If we assume, with many chemists, the nitrogen of these acids to exist in the form of hyponitric acid, the formula of nitrococcusic acid will be represented by

$$2H, C_{16}\left\{\begin{matrix} H_3 \\ 3NO_4 \end{matrix}\right\} O_6.$$

This acid would consequently derive from a non-nitrogenous acid, having the composition expressed by the formula

$$2H, C_{16} H_6 O_6.$$

When I first began this investigation I imagined that a similar relation might exist between nitrococcusic acid and carminic acid; the analysis of these acids, however, as well as the simultaneous production of a large quantity of oxalic acid in its oxidation, showed that this view was erroneous, and that nitrococcusic acid was derived from carminic acid in a more complex manner. Some attempts were made to produce the non-nitrogenous acid, *the coccusic acid*, but unsuccessfully.

The experiments of MM. Cahours and Laurent on the oxidation of the oils of anise and of tarragon (*Oleum dracunculi*) have made us acquainted with anisic acid, the composition of which is

$$C_{16} H_8 O_6.$$

The formula agrees with the composition of the hypothetical hydrided coccusic acid.

Anisic acid, however, as well as nitranisic acid, being monobasic, it was not probable that the further introduction of the elements of hyponitric acid would convert it into a bibasic one; nevertheless, it was my intention to have studied the further action of nitric acid on the acids mentioned, in order to obtain, if possible, trinitranisic acid, and to compare this substance with the acid obtained from carminic acid, when an account of some new experiments of M. Cahours came

under my notice, respecting the action of a mixture of concentrated sulphuric and nitric acids on anisic acid, by which he has succeeded in preparing trinitranisic acid. The experiments of M. Cahours have not yet been published in detail, and from his short account it was not possible to decide on the identity or non-identity of nitrococcusic and trinitranisic acids. A small specimen of anisic acid at my disposal was treated in the manner described by him; after acting for some time water threw down an acid, from the insolubility of which I conclude that these acids are only isomeric.

### INVESTIGATION OF THE MOTHER-LIQUOR FROM WHICH THE CARMINIC ACID HAD BEEN SEPARATED.

On evaporating the mother-liquors of carminic acid, and separating the lead held in solution by means of hydrosulphuric acid, they all gave the following results: on acquiring a syrupy consistence, a white chalk-like matter subsided; this was separated by filtration, and proved to be a new crystalline body. The liquor filtered off from this substance, deposited a small quantity more on further concentration, and could only be dried to a soft tenacious mass, partly soluble in alcohol, the rest being soluble in water. From three pounds of cochineal, five ounces of this soft matter were obtained, showing that the precipitation by a lead-salt had effected the separation of carminic acid from a large quantity of foreign matters. This gelatinous matter appears to be of a complex character, but I have not yet examined it fully.

To purify the chalk-like matter, it was well-washed with cold water and crystallized twice by solution in boiling water and evaporation; it was then dissolved by boiling it in a just sufficient quantity of water; animal charcoal was now added, and the ebullition continued for a few minutes; the solution filtered whilst hot, deposited on cooling, a mass of silky crystalline tufts, completely filling the liquid, and when collected and dried, they aggregated into paper-like masses of a silky aspect. I obtained in three experiments 4 parts of the new body from 1000 of cochineal.

I. 0·4918 grm. of substance, preparation (*a*), dried *in vacuo*, and burnt with protoxide of copper gave:
1·0705 „ of carbonic acid, and
0·2838 „ of water.

II. 0·5680 „ of substance (*b*) gave:
1·2416 „ of carbonic acid, and
0·3160 „ of water.

III. 0·4700 „ of substance (*b*) gave:
1·0210 „ of carbonic acid, and
0·2660 „ of water.

For the latter analysis, I am indebted to the kindness of Mr. Nicholson.

A qualitative examination having pointed out the presence of nitrogen, it was determined by Varrentrapp and Will's method.

IV. 0·5046 grm. of substance (*a*) dried *in vacuo*, and burnt with soda-lime gave:
0·6131 „ of bichloride of platinum and ammonium.
V. 0·5076 „ of substance (*b*) gave:
0·6239 „ of bichloride of platinum and ammonium.

From these numbers the following per centages are calculated:—

| | I. | II. | III. | IV. | V. |
|---|---|---|---|---|---|
| Carbon . . | 59·36 | 59·62 | 59·25 | — | — |
| Hydrogen . | 6·41 | 6·18 | 6·29 | — | — |
| Nitrogen . | — | — | — | 7·62 | 7·71 |

These per centages, translated into the most simple expression, lead to the formula:

$$C_{18}\,H_{11}\,N\,O_6$$

as may be seen from the following table:—

| | Theory. | | Experiment. Mean. |
|---|---|---|---|
| 18 equivs. of Carbon. . . | 108 | 59·668 | 59·41 |
| 11 „ of Hydrogen . | 11 | 6·077 | 6·29 |
| 1 „ of Nitrogen . . | 14 | 7·735 | 7·66 |
| 6 „ of Oxygen . . | 48 | 26·520 | — |
| | 181 | 100·000 | |

Careful and repeated examinations for sulphur proved the absence of this element as a component of the new white substance. I have been unable to produce a compound to control the proposed formula, though several methods were adopted; amongst others, I attempted to form a lead compound by adding acetate of lead to an ammoniacal solution of the substance; I obtained merely a bulky precipitate, consisting of little else than protoxide of lead.

This substance is sparingly soluble in cold water, much more so in boiling water; insoluble in alcohol and ether; soluble in hydrochloric acid, which appears to be driven off by evaporation, leaving

the substance in large crystals. In a large quantity of nitric acid it dissolves with a slight evolution of gas; the solution evaporated spontaneously furnishes long crystals, which are in all probability a new acid; if dissolved in a small quantity of nitric acid, the mixture becomes spontaneously heated, violent action takes place, and the product is lost; frequently the substance becomes blackened into charred masses. It is soluble in ammonia, from which it is again recovered by the evaporation of the ammonia. It is soluble in the fixed alkalies, and is precipitated from these solutions by saturating with an acid.

In a short paper, entitled "Valerianic Acid and a new body from Casein," Baron Liebig* describes a new substance obtained by fusing casein with hydrate of potassa until an evolution of hydrogen takes place along with ammonia. On saturating with acetic acid, the aqueous solution of the fused mass, an aggregate of fine needles was produced, which were purified by repeated solution in carbonate of potassa and reprecipitation by acetic acid. A preliminary analysis led to the formula,

$$C_{16} H_9 N O_5,$$

differing from the result I obtained in the analysis of the white substance from cochineal by two carbon, two hydrogen, and one oxygen. The properties of the two bodies being however so analogous, it is extremely probable that they are identical, a presumption I am supported in by a comparison of a specimen kindly furnished me by Dr. Hofmann;* further investigations will clear up this point: in the meantime I refrain from proposing a name, as Liebig† has lately proposed the name Tyrosine for the substance prepared from casein. As the latter body arises evidently from a process of oxidation, and as I had obtained the first crop of crystals from a liquid from which the colouring matter had been precipitated by the basic nitrate of lead, I thought that this body might owe its formation to the action of the nitric acid liberated by the hydrosulphuric acid; but this supposition proved to be erroneous, for in later experiments, in which acetate of lead had been used, the same body, and in exactly the same quantity, was obtained. From this we may assume that this substance is contained ready-formed in the cochineal insect.

These researches were commenced and prosecuted some time in

* Liebig's Annalen, vol. LVII, p. 127.

† This specimen had been prepared by Baron Liebig himself.—A. W. H.

‡ Researches on the Chemistry of Food, p. 16.

the laboratory of the College; occupying, however, a longer period than was anticipated, they were completed in my own laboratory. During the progress of this investigation, I was much indebted to the friendly advice of Dr. Hofmann, to whom I have great pleasure in expressing my thanks.

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## IX.—*Researches on Cumarine.*

By Hermann Bleibtreu, Esq.

(Read before the Chemical Society of London, May 4th, 1846).

The attention of chemists has long been attracted to the *Asperula odorata*, a plant well known in Germany under the name of 'Waldmeister,' and which in many districts, particularly on the Rhine, is employed in the preparation of the favourite 'Maitrank' or 'Maiwein.'

Many experiments have been made for the purpose of separating and investigating the volatile substance contained in the 'Waldmeister,' to which the 'Maiwein' owes its agreeable odour and flavour.

Some years ago Voget* occupied himself with this subject, and obtained from the 'Waldmeister' a crystalline substance, which he described as possessing the same odour as the Tonka bean and *Melilotus*, and which from his experiments he declared to be benzoic acid.

More lately Kosmann† has published some experiments which led him to the conclusion, that the principle contained in this plant was cumarine, the stearoptene of the Tonka bean. By treating the dried plant with alcohol and ether, evaporating these solvents and boiling the syrupy residue in water, and concentrating, he obtained a crystalline mass, the agreeable odour and pungent taste of which were exactly similar to those of cumarine prepared from the Tonka bean.

The experiments of Kosmann were however purely qualitative. No analysis was made of the crystals obtained from the 'Waldmeister,' which alone could have determined the point; nor was an experiment tried as to the ready transformation of cumarine into salicylic acid,

* Generalbericht des König. Preus. Rhein. Medicinalcol. ueber das Jahr, 1835. Coblenz bei Kehr, p. 240.

† Journ. de Pharm., 3 sér. t. v. p. 393. Ann. der Chem. und Pharm., B. LII, p. 387.

so easily recognised by its reaction with the salts of sesquioxide of iron, and from which a tolerable conclusion might have been drawn.

It hence appeared to me desirable to establish, by a more exact investigation, the observations of Kosmann.

The following experiments instituted for this purpose, and including a revision of the investigation of cumarine by Delalande, were commenced in the laboratory of my friend Professor Hofmann in Bonn, and finished in that of the Royal College of Chemistry in London, to which I accompanied him in the capacity of assistant on his election as Professor to the latter.

I have much pleasure in embracing this opportunity to express my thanks to Dr. Hofmann for his instructions in organic researches generally, and more particularly for his assistance in the present investigation.

### INVESTIGATION OF THE CRYSTALS FROM 'ASPERULA ODORATA.'

For the preparation of this substance I proceeded in the following manner:—

A quantity of 'Waldmeister,' collected shortly before and during flowering, was dried in the air and digested for some time with spirits of wine; the alcohol was distilled off from the greenish-brown solution in a water-bath, and the dark brown residue evaporated to the consistency of syrup. The distilled alcohol had an aromatic odour, and from the last more watery portion small crystalline plates were gradually deposited.

The syrup was boiled with water, and the brown solution, separated by filtration from the insoluble matters, consisting of chlorophylle, &c., agitated with ether. On distilling off the ether there remained a yellow substance, possessing the appearance and odour of honey, from which, after some time, a considerable quantity of yellow crystalline needles separated, which on heating with water to 50° C. collected at the bottom of the vessel into a melted mass, and were dissolved on raising the temperature to the boiling-point. From this solution, which on cooling became milky, crystals of an inch in length were gradually deposited, which were purified by repeated crystallizations. After being thrice recrystallized the crystals were of a pure white colour, but deposited some brownish flakes when fused at a gentle heat. On repeating the recrystallization once more, the substance remained quite unchanged in colour after fusing, and could now be considered as quite pure and proper for analysis.

Before proceeding to the analysis, I endeavoured to convert a small

portion of the substance into salicylic acid. A few crystals were dissolved in strong potassa ley, evaporated till the yellow colour at first produced had disappeared, and then heated somewhat stronger. The solid residue was saturated with hydrochloric acid and agitated with ether. The ethereal solution, evaporated to drive off the ether, gave with sesquichloride of iron the beautiful violet colour so characteristic of salicylic acid.

The analysis of the fused crystals, in one case with protoxide of copper, in the other with chromate lead, gave the following results :—

I. 0·3276 grm. of substance gave:
0·8821 „ of carbonic acid, and
0·1267 „ of water.
II. 0·2607 „ of substance gave:
0·7105 „ of carbonic acid, and
0·1043 „ of water.

Per centage composition:

| | I. | II. |
|---|---|---|
| Carbon . . . . | 73·63 | 74·33 |
| Hydrogen . . . | 4·31 | 4·44 |

According to the experiments of Delalande the formula of cumarine is

$$C_{18} H_7 O_4,$$

giving the following per centage, which I compare with the mean of his analyses calculated with the new atomic weight of carbon as determined by Dumas,

| | Theory. | | Mean of Delalande's experiments. |
|---|---|---|---|
| 18 equivs. of Carbon . . | 108 | 73·47 | 72·91 |
| 7 „ of Hydrogen . . | 7 | 4·76 | 4·73 |
| 4 „ of Oxygen . . | 32 | 21·77 | — |
| 1 equiv. of Cumarine. . | 147 | 100.00 | |

The result of my analyses approach near enough to those of Delalande to prove the identity of cumarine and the substance obtained from *Asperula odorata*. A comparison however of the amount of carbon and hydrogen shows, particularly in the former, a sufficient deviation to throw a doubt on the absolute number of equivalents. The circumstance moreover of the near agreement, nay even of the excess of the quantity of hydrogen calculated over that

obtained in the mean of Delalande's experiments, whilst in analysis the reverse is almost invariably the case, gave me grounds to doubt the correctness of his formula, and induced me to repeat the investigation of cumarine obtained from the Tonka bean.

### INVESTIGATION OF CUMARINE FROM THE TONKA BEAN.

The following appeared to be the best method of preparing cumarine from the Tonka beans.

The beans, finely cut or pounded, were digested for some time with strong alcohol. The syrupy mass remaining after distilling off the alcohol, became on cooling a solid magma of crystals of cumarine, which could be easily purified by treatment with animal charcoal and repeated crystallizations. By proceeding in this manner it is very easy to separate a fatty oil, which is contained in considerable quantity in the Tonka bean. This body is colourless, inodorous, soluble in ether, insoluble in alcohol and water, and possesses the property of dissolving cumarine in considerable quantity.

The process of treating the beans with ether, or directly extracting the cumarine by boiling in water, is much inferior, as the greater part of the oil is also removed with it, and can afterwards be separated only with difficulty. In the fresh bean the cumarine appears to be contained in solution in this oil, from which it gradually separates in the form of pure white crystals, and is found collected particularly between the cotyledons and on their surfaces under the skin.

Two combustions of cumarine from the Tonka bean gave the following results:—

I. 0·4870 grm. of substance gave:
1·3209 „ of carbonic acid, and
1·1882 „ of water.
II. 0·6423 „ of substance gave:
1·7361 „ of carbonic acid, and
0·2416 „ of water.

These numbers correspond to the following per centage:

| | I. | II. |
|---|---|---|
| Carbon . . . . | 73·97 | 73·72 |
| Hydrogen . . . | 4·29 | 4·18 |

These two analyses correspond exactly with that of the cumarine obtained from *Asperula odorata*. In all there is a larger amount of

carbon and a smaller quantity of hydrogen than in the analyses of Delalande.

The expression corresponding to the mean of my experiments is

$$C_{18}\,H_6\,O_4,$$

which contains 1 equivalent of hydrogen less than Delalande's formula, as is seen in the following table containing both the experimental and theoretical numbers:

| | | Theory. | | Bleibtreu. | Delalande. |
|---|---|---|---|---|---|
| 18 equivs. | of Carbon . | 108 | 73·97 | 73·91 | 72·91 |
| 6 „ | of Hydrogen . | 6 | 4·11 | 4·30 | 4·73 |
| 4 „ | of Oxygen . | 32 | 21·97 | — | — |
| 1 equiv. | of Cumarine . | 146 | 100·00 | | |

These experiments leave no doubt as to the identity of the crystalline principle of the *Asperula* and the stearoptene of the Tonka bean.

The delightful aroma which characterizes 'Maiwein' is entirely due to this substance. A liquor artificially prepared with the stearoptene of the Tonka bean met with the warmest approbation from a number of teachers and students in the University of Bonn.

### PRODUCTS OF DECOMPOSITION OF CUMARINE.

The new formula for cumarine I endeavoured to control by investigating the products of decomposition of this body.

Delalande obtained by heating cumarine with concentrated potassa a peculiar acid,

$$H\,C_{18}\,H_7\,O_6,$$

which he described under the name of cumaric acid. It is this acid which, according to his experiments, is converted by further treatment with potassa into salicylic acid, the remarkable compound first obtained by Piria as a product of the decomposition of salicine, and to which the attention of chemists has more lately been attracted by the beautiful researches of Cahours on the "Oil of the *Gaultheria procumbens*."

Delalande expresses these transformations by the following formulæ:—

$$\underbrace{C_{18}\,H_7\,O_4}_{\text{Cumarine.}};\; + 2\,HO = \underbrace{H\,C_{18}\,H_7\,O_6}_{\text{Cumaric acid.}} + H.$$

$$\underbrace{H\,C_{18}\,H_7\,O_6}_{\text{Cumaric acid.}} = \underbrace{H\,C_{14}\,H_5\,O_6}_{\text{Salicylic acid.}} + C_4\,H_2.$$

On repeating the experiments of Delalande I arrived at the following results.

Cumarine dissolves readily in potassa and forms with it a yellowish solution, from which acids reprecipitate cumarine unchanged. It is only attacked by heating it with a concentrated ley, to which pieces of solid potassa have been added. From this solution hydrochloric acid precipitates a substance totally differing in its character from cumarine, and which is evidently the acid described by Delalande.

*However by careful treatment of cumarine with potassa, I have never been able to observe a disengagement of hydrogen.*

The acid prepared in the above manner may contain traces of salicylic acid. After removal of the chloride of potassium and the excess of hydrochloric acid, and dissolving in water, it gave indeed, with salts of sesquioxide of iron, the violet colour characteristic of salicylic acid. Delalande however states expressly in his memoir, that this reaction is not only due to salicylic, but also to cumaric acid. This remark is evidently erroneous, for on washing with water the acid once crystallized, this reaction became weaker and weaker, and finally totally disappeared on a second crystallization. The violet colour produced by the sesquichloride of iron was consequently due to the presence of a small quantity of salicylic acid, the formation of which cannot easily be prevented.

The acid prepared in the above manner, and freed from salicylic acid as much as possible by repeated recrystallizations, may still contain traces of undecomposed cumarine, from which it must be separated; for this purpose it was dissolved in ammonia. From the yellow solution the excess of ammonia was expelled by boiling, and the yellowish-white silver-salt produced by the addition of nitrate of silver was collected on a filter and washed with water, then with alcohol, and finally with ether. After such a treatment the silver-salt could not contain any trace of cumarine, and the acid now separated by hydrochloric acid, extracted by ether, and recrystallized from boiling water after distilling off the ether, could be regarded as *pure cumaric acid.*

With salts of sesquioxide of iron it now produced no colour whatever. Pure cumaric acid possesses the following properties. It is readily soluble in alcohol and ether, and crystallizes from boiling water in white brittle crystals. It has a decidedly acid reaction, and

expels carbonic acid from its salts. Its point of fusion is near 190° C. If more strongly heated, it is partly decomposed into white shining crystals, which sublime, and a brownish residue.

The cumarate of ammonium is not precipitated by a salt of barium; but a white powdery insoluble precipitate is obtained by the addition of acetate of lead.

A combustion with chromate of lead of cumaric acid, dried at 100° C., gave the following results:—

0·3415 grm. of substance gave:
0·8215 „ of carbonic acid, and
0·1532 „ of water.

Per centage composition:

| | |
|---|---|
| Carbon . . . . | 65·61 |
| Hydrogen . . . . | 4·98 |

These numbers correspond exactly to the formula of Delalande for this acid:

$$HC_{18}H_7O_6.$$

The following are the experimental and theoretical numbers:

| | Theory. | | Bleibtreu. | Delalande. |
|---|---|---|---|---|
| 18 equivs. of Carbon . | 108 | 65·85 | 65·61 | 65·34 |
| 8 „ of Hydrogen | 8 | 4·88 | 4·98 | 5·05 |
| 6 „ of Oxygen . | 48 | 29·27 | — | — |
| 1 eq. of Cumaric Acid | 164 | 100·00 | | |

To control this formula, I also analysed the silver-salt of Delalande. It was obtained, as above stated, by dissolving cumaric acid in ammonia and precipitating with nitrate of silver. It is a light yellow, almost white salt, quickly settling to the bottom of the vessel. It was dried at 100° C.

I. 0·8237 grm. of the salt gave:
0·3287 „ of silver.
II. 0·5181 „ of salt gave:
0·2049 „ of silver.
III. 0.5850 „ of cumarate of silver gave:
0·8580 „ of carbonic acid, and
0·1392 „ of water.

Per centage composition:

| | I. | II. | III. |
|---|---|---|---|
| Silver . . . | 39·90 | 33·55 | — |
| Carbon . . . | — | — | 40·00 |
| Hydrogen . . | — | — | 2·64 |

These results correspond exactly with those of Delalande, and lead to the following formula:

$$Ag, C_{18} H_7 O_6.$$

The calculated and experimental numbers are as follows:

| | Theory. | | Experiment. | |
|---|---|---|---|---|
| | | | Bleibtreu. | Delalande. |
| 1 equiv. of Silver . . | 108 | 39·84 | 39·72 | 40·00 |
| 18 equivs. of Carbon . . | 108 | 39·86 | 40·00 | 39·82 |
| 7 „ of Hydrogen . | 7 | 2·58 | 2·64 | 2·62 |
| 6 „ of Oxygen . . | 48 | 17·72 | — | — |
| 1 equiv. of Silver-salt | 271 | 100·00 | | |

FORMATION OF CUMARIC AND SALICYLIC ACID FROM CUMARINE.

From the above experiments, it is evident that the formula given by Delalande to cumaric acid must be regarded as the correct one. The representation, however, of the formation of this acid, to which this chemist was led by the incorrect formula of cumarine, requires correction. The formation of cumaric acid does not depend upon a decomposition of water, the oxygen of which is added to the elements of cumarine, but simply on the assumption of 2 equivalents of this body, exactly analagous to the formation of benzilic acid from benzile or isatinic acid from isatine.

$$\underbrace{C_{28} H_{10} O_4}_{\text{Benzile.}} + 2HO = \underbrace{H\, C_{28} H_{11} O_6}_{\text{Benzilic acid.}}$$

$$\underbrace{C_{16} H_5 NO_4}_{\text{Isatine.}} + 2HO = \underbrace{H\, C_{16} H_6 NO_6}_{\text{Isatinic acid.}}$$

$$\underbrace{C_{18} H_6 O_4}_{\text{Cumarine.}} + 2HO = \underbrace{H\, C_{18} H_7 O_6}_{\text{Cumaric acid.}}$$

It is not requisite even to fuse the cumarine with caustic potassa: by the employment of an alcoholic solution of potassa it is also transformed, though very slowly, into cumaric acid. In this latter case there remains always, even after long treatment, a large portion of cumarine undecomposed.

The evolution of hydrogen mentioned by Delalande, and which, as already stated, I never observed in a well-conducted experiment, arose evidently from the formation of salicylic acid by the further action of the potassa on the cumaric acid. This view is supported by the

violet-coloured reaction with sesquichloride of iron described by him, and which, as I have shown, does not belong to cumaric acid. His cumaric acid evidently contained a small quantity of salicylic acid.

From the aforesaid grounds, the view taken by Delalande on the transformation of cumaric into salicylic acid must also be modified. According to him, no evolution of hydrogen takes place in this formation, but an aromatic gas is disengaged, burning with a coloured flame, and which he regarded as a carbo-hydrogen, $C_4 H_2$, representing the difference of constitution between the two acids—

$$\underbrace{H\ C_{18} H_7 O_6}_{\text{Cumaric acid.}} - \underbrace{C_4 H_2}_{\text{Aromatic gas.}} = \underbrace{H\ C_{14} H_5 O_6}_{\text{Salicylic acid.}}$$

This manner of viewing the reaction is evidently incorrect. If pure cumarine is fused with hydrate of potassa, the latter is almost entirely transformed into carbonate after the formation of the salicylic acid. The carbon therefore separates in the form of an oxygenated compound.

I have made no quantitative experiment on this point; but all my observations tend to prove that the formation of the salicylic acid may be represented by the following equation:—

$$\underbrace{H\ C_{18} H_7 O_6}_{\text{Cumaric acid.}} + 8HO = \underbrace{H\ C_{14} H_5 O_6}_{\text{Salicylic acid.}} + 4CO_2 + 10H.$$

As to the aromatic gas burning with a brilliant flame, which is evolved in the latter stages, it is no carbo-hydrogen, but the oxide of a carbo-hydrogen, viz. phenol, arising by a further loss of carbonic acid from the salicylic acid already formed.

$$\underbrace{H\ C_{14} H_5 O_6}_{\text{Salicylic acid.}} - 2CO_2 = \underbrace{C_{12} H_6 O_2}_{\text{Phenol.}}$$

The vapour of this compound imparts a yellow colour to the flame of the hydrogen.

## NITROCUMARINE.

Delalande has studied the action of nitric acid on cumarine. The correction of the formula of the latter body made it desirable to repeat also this experiment, as it was probable that a corresponding change would likewise require to be made in that of the product of decomposition.

Cumarine dissolves with considerable elevation of temperature, but

without almost any evolution of red fumes in cold fuming nitric acid. On addition of water a white cheesy precipitate is obtained, which quickly settles to the bottom. The fluid possesses a deep yellow colour. After washing with cold water, the precipitate was dissolved in boiling alcohol, from which, on cooling, white shining silky crystals separated. In this treatment with nitric acid a strong heat is to be particularly avoided, as the whole of the cumarine is converted into nitropicric acid if the fluid is allowed to boil. The formation of a small quantity of the latter acid can never be completely avoided, and from its presence arises the yellow colour of the mother-liquor.

To the above product of decomposition Delalande gave the name nitrocumarine. In accordance with his view of the composition of cumarine, he assigned to it the following formula:—

$$C_{18}\left\{\begin{matrix}H_6\\NO_4\end{matrix}\right\}O_4.$$

It is scarcely necessary to remark, that this formula must be changed into

$$C_{18}\left\{\begin{matrix}H_5\\NO_4\end{matrix}\right\}O_4,$$

as is shown by the analysis of the fused crystals with oxide of copper.

0·5675 grm. of substance gave:
1·1657 „ of carbonic acid, and
0·1348 „ of water.

In per centage,

| | |
|---|---|
| Carbon . . . . | 56·02 |
| Hydrogen . . . . | 2·64 |

which, compared with the per centage calculated from the new formula, is:

| | Theory. | | Experiment. |
|---|---|---|---|
| 18 equivs. of Carbon . . . . . | 1350·00 | 56·54 | 56·02 |
| 5 „ of Hydrogen . . . . | 62·50 | 2·62 | 2·64 |
| 1 equiv. of Nitrogen . . . . | 175·25 | 7·34 | — |
| 8 equivs. of Oxygen . . . . . | 800·00 | 33·50 | — |
| 1 equiv. of Nitrocumarine . . . | 2387·75 | 100·00 | |

Delalande's formula requires the following per centage:

| | |
|---|---|
| Carbon . . . | 56·24 |
| Hydrogen . . | 3·12 |

The determination of the hydrogen, on which the formula more directly depended, leaves no doubt as to the choice of the two. The formation of nitrocumarine is analogous to that of nitrobenzol, nitrostyrol, &c.:

$$\underbrace{C_{18}H_6O_4}_{\text{Cumarine.}} + H\,NO_6 = \underbrace{C_{18}\left\{\begin{matrix}H_5\\NO_4\end{matrix}\right\}O_4}_{\text{Nitrocumarine.}} + 2\,HO.$$

I have but little to add to Delalande's description of the properties of this body. Nitrocumarine dissolves with difficulty in water, alcohol and ether, and crystallizes in fine needles from these solvents as soon as the temperature falls a little below their boiling-points. Its point of fusion is about 170° C.; heated beyond this it sublimes without decomposition in the form of large white crystals of the lustre of mother-of-pearl.

Nitrocumarine forms with alkalies a solution of a deep yellow, almost red colour, which disappears on the addition of an acid, with separation at the same time of a white crystalline matter. This reaction was further examined in the hopes of obtaining an acid corresponding to nitrocumarine, viz. nitrocumaric acid.

For this purpose nitrocumarine was boiled for some time in an alcoholic solution of potassa; the potassa compound formed, was decomposed by hydrochloric acid, and the precipitate after removal by washing of the chloride of potassium, recrystallized from boiling alcohol.

To free the crystals (which I regarded as nitrocumaric acid) from any nitrocumarine which might still be mixed with them, they were dissolved in ammonia when boiled, in order to remove any excess of the latter; a portion of the substance was then deposited in the form of white crystalline flakes. That these crystals were only nitrocumarine was proved by the absence of any trace of ammonia on gently heating with potassa.

The filtered solution, which was neutral, gave with nitrate of silver a beautiful orange-yellow, with acetate of lead an orange precipitate. Both compounds were soluble in a considerable quantity of water, forming a light yellow solution, but less so in alcohol and ether; so that they could be purified by boiling with these menstrua. I have analysed these compounds as well as the substance separated from them by acids.

The lead and silver precipitates are direct compounds of nitro-

cumarine with the oxides of the metals, and the electro-negative bodies obtained from them is pure *nitrocumarine*.

The combustion of this substance with oxide of copper gave the following results:—

0·2567 grm. of substance gave:
0·5338 „ of carbonic acid, and
0·0672 „ of water.

In per centage,—

| | |
|---|---|
| Carbon . . . . . | 56·71 |
| Hydrogen . . . . | 2·90 |

Nitrocumarine contains, as before stated,

| | |
|---|---|
| Carbon . . . . . | 56·54 |
| Hydrogen . . . . | 2·62 |

whilst nitrocumaric acid,

$$H\,C_{18}\left\{\begin{matrix}H_6\\NO_4\end{matrix}\right\}O_6,$$

corresponding to cumaric acid, is represented by the following widely differing per centage,—

| | |
|---|---|
| Carbon . . . . | 51·67 |
| Hydrogen . . . . | 3·35 |

The lead compound was dried at 100°, decomposed by nitric acid, and precipitated by dilute sulphuric acid.

0·6557 grm. of substance gave:
0·5548 „ of sulphate of lead.

In per centage: protoxide of lead 62·27, which corresponds to a formula approaching nearly to

$$3\,PbO,\,C_{18}\left\{\begin{matrix}H_5\\NO_4\end{matrix}\right\}O_4,$$

of which the calculated per centage of lead is 63·66.

The silver compound undergoing decomposition at the temperature of the water-bath was dried *in vacuo*.

A determination of the silver was made by burning the compound, in which however a slight loss was incurred by deflagration.

0·3037 grm. of substance gave:
0·1526 grm. of silver.

In per centage: protoxide of silver 53·97, which corresponds to a compound of nitrocumarine and 2 equivalents of protoxide of silver,

$$2\,AgO,\,C_{18}\left\{\begin{matrix}H_5\\NO_4\end{matrix}\right\}O_4,$$

of which the calculated per centage of protoxide silver is 54·83.

The same lead and silver compounds are also obtained by adding a lead or silver-salt to nitrocumarine simply dissolved in ammonia. From these experiments it is evident that nitrocumarine undergoes no decomposition on boiling in an alcoholic solution of potassa. Further experiments must decide whether nitrocumaric acid can be obtained by careful fusion of nitrocumarine with caustic alkalies, or directly from cumaric acid, by proper treatment with nitric acid.

The formation of this acid would have been of some interest. The late investigations of Zinin have shown us that acids of this class, under the influence of reducing agents, as hydrosulphuric acid, &c., exchange 4 equivalents of oxygen for 2 of hydrogen, or, in other words, 1 equivalent of hyponitric acid for 1 equiv. of amidogen.

Whilst *bases* are thus formed from nitro-carbohydrogens, the *electro-negative* character of the nitro-acids remains unchanged. Benzoic acid, for example, treated in the above manner, gives the following series:

| | |
|---|---|
| Benzoic acid . . | $H\,C_{14}\,H_5\,O_4$ |
| Nitrobenzoic acid . | $H\,C_{14}\left\{\begin{matrix}H_4\\NO_4\end{matrix}\right\}O_4$ |
| Amidobenzoic acid<br>Benzamidic acid | $H\,C_{14}\left\{\begin{matrix}H_4\\Ad\end{matrix}\right\}O_4$ |

Were it possible to form from cumaric acid a similar series:

| | |
|---|---|
| Cumaric acid . . | $H\,C_{18}\,H_7\,O_6$ |
| Nitrocumaric acid . | $H\,C_{18}\left\{\begin{matrix}H_6\\NO_4\end{matrix}\right\}O_6$ |
| Amidocumaric acid | $H\,C_{18}\left\{\begin{matrix}H_6\\Ad\end{matrix}\right\}O_6$ |

there was a hope of thus producing, artificially, hippuric acid, for amidocumaric acid is identical in composition with hippuric acid.

$$\underbrace{H\,C_{18}\left\{\begin{matrix}H_6\\Ad\end{matrix}\right\}O_6}_{\text{Amidocumaric acid.}} = \underbrace{H\,C_{18}\,H_8\,NO_6}_{\text{Hippuric acid.}}$$

Whether indeed such a relation exists has to be decided by further researches. In the following I may briefly notice some experiments partly made with this intention, but which as yet have not led to decided results.

It was not impossible that by the direct action of reducing agents on nitrocumarine an amidocumarine could have been formed, which

by subsequent treatment with alkalies might have been converted into the desired acid. For this purpose a quantity of nitrocumarine was mixed with alcohol, into which ammoniacal gas was passed till the whole was dissolved, and then submitted for a considerable time to a current of hydrosulphuric acid.

The fluid, from which, even after several days, no sulphur had been separated, was distilled in a retort till no more sulphide of ammonium passed over. On exposure to the air in a flat vessel it now deposited a yellow, slimy, tenacious mass, the characteristic garlic smell of which led to the suspicion of its containing sulphur.

By longer exposure to the air this slimy mass assumed the consistency of wax, and finally hardened into a resinous-like body, insoluble in water, but tolerably soluble in alcohol and ether.

Ammonia also dissolved this substance with separation of a little sulphur. On boiling this solution a portion of the compound was again deposited as the ammonia was driven off.

The filtered solution, which was nearly neutral, gave, on the addition of hydrochloric acid, a brown amorphous precipitate, and with lead and silver-salts light yellow compounds.

Want of substance has as yet prevented me from making a thorough investigation of these bodies. I may here only mention, that the yellow lead compound gave 34·21 per cent. of lead, and that the organic substance separated from it contained 9·55 per cent. of sulphur.

### CUMARINE IN ANTHOXANTHUM ODORATUM.

The detection of cumarine in *Asperula odorata* led to the suspicion that this principle might probably be contained in other plants in which benzoic acid has been hitherto supposed to have been met with.

Some time ago Guillemette* showed that the crystalline principle of the *Melilotus officinalis*, which was formerly believed to be benzoic acid, was identical with cumarine.

This observation was completely confirmed by some experiments made by me with the crystalline principle of this plant, which was easily converted into salicylic acid.

Of the other plants said to contain benzoic acid, I have as yet been able to obtain only *Anthoxanthum odoratum* (Ruchgras), a grass to which is attributed the agreeable smell of new hay, and which is to be found in most meadows.

* Ann. der Chim. und Pharm., B. xiv, p. 324. Journ. de Pharm., 1835, p. 172.

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To detect the cumarine I proceeded in the same manner as with the *Asperula odorata*, and obtained white crystals, which in odour and taste, as well as in all other properties, were not to be distinguished from cumarine. On fusing these crystals with hydrate of potassa, testing the product of decomposition with sesquichloride of iron, the intense violet colour produced by the salicylic acid which had been formed showed with certainty the presence of cumarine in the original substance.

The hippuric acid found in the urine of graminivorous animals has been supposed to derive in various ways its origin from the benzoic acid imagined to exist in the *Anthoxanthum odoratum*. The transformation experienced by that acid in the animal economy appeared to support this view in a remarkable manner.

It would be desirable to try whether with cumarine the same change takes place. The narcotic action of this substance on the animal organism, however, has prevented me from making direct experiments.

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## X.—*On the Composition of Caffeine and some of its Compounds.*

By Edward Chambers Nicholson, Esq.

(Read before the Chemical Society of London, February 15, 1847.)

Caffeine was first analysed by Professors Liebig and Pfaff,* in 1832. The result of this investigation was confirmed by a subsequent analysis of Professor Wöhler.†

In 1838, Professor Liebig induced M. Jobst‡ to analyse theine, who proved this body to be identical with caffeine. His analyses gave the same results as those of his predecessors. The same remark applies to the experiments of Mulder§ on theine, and also to an analysis which M. Martius‖ made of guaranine, a substance, the identity of which with caffeine and theine had previously been pointed out by Berthemot and Dechastelus.¶ Lately, Dr. Stenhouse,** when examining Paraguay tea, has also made some analyses of theine.

The following table, in which I have recalculated these analyses,

* Liebig's Annalen, I, 17 † Ibid. ‡ Ibid. xxv, 63.
§ Bulletin des Sciences Phys. et Nat. de Neerlande, 1838, p. 32.
‖ Liebig's Annalen, xxxvi, 93. ¶ Ibid. xxxvi, 90.
** Transactions of the Chemical Society, vol. I, pp. 215, 237.

according to the atomic weights, carbon 6 and hydrogen 1, allows a comparison to be made of the results obtained by these chemists.

MEAN OF THE ANALYSES.

| | Caffeine. | | Theine. | | | Guaranine. |
|---|---|---|---|---|---|---|
| | Liebig & Pfaff. | Wöhler. | Mulder. | Jobst. | Stenhouse. | Martius. |
| Carbon . . | 49·30 | 49·25 | 49·18 | 49·47 | 48·95 | 49·23 |
| Hydrogen . | 5·22 | 5·43 | 5·49 | 5·20 | 5·15 | 5·08 |
| Nitrogen . | 28·86 | — | 28·53 | 28·90 | — | 28·83 |

The most simple expression which can be deduced from these numbers is,

$$C_8 H_5 N_2 O_2.$$

Stenhouse's analysis, however, of the platinum compound proves that this formula must be doubled, and that the atom of caffeine or theine is,

$$C_{16} H_{10} N_4 O_4.$$

The theoretical numbers of this formula are the following:

| | | | |
|---|---|---|---|
| 16 equivs. | of Carbon . . . | 96 | 49.48 |
| 10 „ | of Hydrogen . . | 10 | 5·15 |
| 4 „ | of Nitrogen . . | 56 | 28·86 |
| 4 „ | of Oxygen . . . | 32 | 16·51 |
| 1 equiv. | of Caffeine . . . | 194 | 100·00 |

From these numerous experiments, the composition of caffeine might have been considered as perfectly established. In a recent investigation of coffee, however, M. Payen* states that he has obtained results which differ very sensibly from those obtained by his predecessors, and which he has translated into the formula

$$C_{16} H_{10} N_4 O_3,$$

which contains 1 equiv. of oxygen less than the formula up to the present time admitted.

The theoretical numbers of Payen's formula are:

| | | | |
|---|---|---|---|
| 16 equivs. | of Carbon . . . | 96 | 51·43 |
| 10 „ | of Hydrogen . . | 10 | 5·35 |
| 4 „ | of Nitrogen . . . | 56 | 30·34 |
| 3 „ | of Oxygen . . . | 24 | 12·88 |
| 1 equiv. | of Caffeine . . . | 186 | 100·00 |

* Comptes Rendus de l'Académie, tome xxiii, 8.

We observe here a difference of 2 per cent. of carbon, which M. Payen has obtained over the results of the above-mentioned chemists.

In order to elucidate this discrepancy, Dr. Hofmann induced me to make some experiments under his direction, partly with a quantity of beautiful caffeine which he gave me,* and partly with a specimen which I have prepared myself.

### CAFFEINE.

To ensure perfect purity of the substance, it was crystallized three times from dilute alcohol, washed and dried. Thus purified, it formed very beautiful long white prisms, perfectly transparent when dried in the air, but which became opaque if exposed to a higher temperature. The crystals dried in the water-bath lost no weight when kept in an air-bath for four hours at a temperature of 130° C.

The specimen which I had prepared myself was obtained from Costa Rico coffee, by boiling the bruised seed in water, precipitating the decoctions by basic acetate of lead, and treating the filtrate with hydrosulphuric acid; after the whole of the lead had been removed, I evaporated the liquid to dryness in a water-bath, in order to get rid of acetic acid, and dissolved the residue in a small quantity of boiling water: upon cooling, the caffeine crystallized out, of a dark colour, and very impure. To purify it, it was washed and recrystallized three times from water, and finally from alcohol. It was then perfectly white, and had exactly the same appearance as the specimen which I obtained from Dr. Hofmann.

By combustion with chromate of lead, the following results were obtained:

I. 0·3827 grm. of substance, dried at 100° C. and burnt with chromate of lead, gave:
0·6948 „ of carbonic acid, and
0·1800 „ of water.

II. 0·417 „ of substance, burnt with chromate of lead and chlorate of potassa, gave:
0·7552 „ of carbonic acid, and
0·1965 „ of water.

* I owe this specimen, of great beauty, to the well-known kindness of Mr. E. Merck, of Darmstadt.—A. W. H.

III. 0·3934 grm. of substance of my own preparation gave:
0·7123 „ of carbonic acid, and
0·1878 „ of water,

which calculated in 100 parts gives:

| | I. | II. | III. |
|---|---|---|---|
| Carbon . . . | 49·51 | 49·39 | 49·37 |
| Hydrogen . . | 5·22 | 5·23 | 5·30 |

agreeing with Professor Liebig's formula, as is seen by the following:

| | | Theory. | | Mean of the experiments. |
|---|---|---|---|---|
| 16 equivs. | of Carbon . . . | 96 | 49·48 | 49·42 |
| 10 „ | of Hydrogen . . | 10 | 5·15 | 5·28 |
| 4 „ | of Nitrogen . . . | 56 | 28·86 | — |
| 4 „ | of Oxygen . . . | 32 | 16·51 | — |
| 1 equiv. | of Caffeine . . . | 194 | 100·00 | |

### CAFFEINE AND BICHLORIDE OF PLATINUM.

On precipitating a solution of caffeine in hydrochloric acid with bichloride of platinum, as Dr. Stenhouse has shown, a precipitate of an orange-yellow colour is obtained. If the two solutions are mixed hot, the fluid on cooling deposits the compound in beautiful granular crystalline tufts, which, when thrown on a filter and washed with alcohol, are perfectly pure. This double salt is only sparingly soluble in alcohol, ether, and water. It does not alter when exposed to light, nor does it lose in weight when kept at 100° C. for a considerable time.

The analyses of salts, all prepared at different periods and dried at 100° C., gave the following results:

I. 0·5382 grm. of substance, burnt with chromate of lead gave:
0·4765 „ of carbonic acid, and
0·1387 „ of water.
II. 0·4881 „ of substance gave:
0·1196 „ of platinum.
III. 0·4779 „ of substance gave:
0·1172 „ of platinum.
IV. 0·6022 „ of substance gave:
0·1482 „ of platinum.
V. 0·5781 „ of substance gave:
0·1425 „ of platinum.

VI. 0·5246 grm. of substance gave:
0·1293 „ of platinum.
VII. 0·3847 „ of substance, made of caffeine of my own preparation, gave:
0·0945 „ of platinum,
These analyses give the following per centages:

| | I. | II. | III. | IV. | V. | VI. | VII. |
|---|---|---|---|---|---|---|---|
| Carbon | 23·80 | — | — | — | — | — | — |
| Hydrogen | 2·86 | — | — | — | — | — | — |
| Platinum | — | 24·51 | 24·52 | 24·60 | 24·64 | 24·64 | 24·56 |

leading exactly to the formula given by Dr. Stenhouse, viz.

$$C_{16}\,H_{10}\,N_4\,O_4,\,HCl,\,Pt\,Cl_2,$$

as is seen when placed in comparison with the calculated numbers.

| | | Theory. | | Mean of my experiments. | Dr. Stenhouse's mean. |
|---|---|---|---|---|---|
| 16 equivs. | of Carbon | 96·0 | 23·97 | 23·80 | 24·22 |
| 11 „ | of Hydrogen | 11·0 | 2·74 | 2·86 | 2·89 |
| 4 „ | of Nitrogen | 56·0 | 13·98 | — | — |
| 4 „ | of Oxygen | 32·0 | 8·02 | — | — |
| 3 „ | of Chlorine | 106·5 | 26·59 | — | — |
| 1 „ | of Platinum | 98·9 | 24·70 | 24·58 | 24·49 |
| 1 equiv. | of Caffeine and Bichloride of Platinum | 400·4 | 100·00 | | |

The analysis of caffeine, as well as that of the platinum compound, agree so perfectly with the numbers of Professor Liebig's formula, that there can be no doubt about its accuracy.

Assuming 1 equiv. of oxygen less in the equivalent of caffeine, as is proposed by M. Payen, the platinum compound should contain not less than 24·46 per cent. of carbon and 25·12 of platinum. Now three determinations by Dr. Stenhouse, and six which I have made, never gave more than 24·64 per cent., that is, 0·6 per cent. less of platinum.

Not satisfied, however, with these proofs, I have tried to find some other compounds by which the atomic weight of caffeine could be determined with equal accuracy.

In what follows, a description of several new double salts of caffeine will be given, the analyses of which correspond equally well with the original formula of this substance.

### CAFFEINE AND NITRATE OF SILVER.

This compound is obtained when a solution of nitrate of silver is added in excess to an aqueous or alcoholic solution of caffeine. If the solutions are concentrated, it falls down in white hemispherical nodules, which adhere firmly to the side of the vessel.

When washed with water and crystallized from alcohol, it is absolutely pure. This compound is indistinctly crystalline, of a perfectly white colour, and if dry undergoes no change when exposed to light, but if moist acquires a purplish hue. It is very soluble in hot water and alcohol, sparingly soluble in cold, and may be boiled in either solvent without undergoing decomposition. It loses no weight in the water-bath, but at a higher temperature it is decomposed, caffeine sublimes, and metallic silver is left.

When burnt with chromate of lead:

I. 0·4514 grm. of substance gave:
0·4345 „ of carbonic acid, and
0·1162 „ of water.
II. 0·2500 „ of substance gave:
0·0744 „ of silver.
III. 0·2716 „ of substance gave:
0·0810 „ of silver,

which give the following per centages:

| | I. | II. | III. |
|---|---|---|---|
| Carbon . . . | 26·45 | — | — |
| Hydrogen . . | 2·86 | — | — |
| Silver . . . | — | 29·76 | 29·82 |

and the formula:

$$C_{16}\,H_{10}\,N_4\,O_4 + Ag,\,NO_6,$$

as may be seen by the following calculation:

| | | Theory. | | Experiment. |
|---|---|---|---|---|
| 16 equivs. | of Carbon . . | 96 | 26·37 | 26·45 |
| 10 „ | of Hydrogen . | 16 | 2·74 | 2·86 |
| 5 „ | of Nitrogen . . | 70 | 19·23 | — |
| 10 „ | of Oxygen . . | 80 | 22·00 | — |
| 1 „ | of Silver . . . | 108 | 29·66 | 29·79 |
| 1 equiv. | of Silver-salt . . | 364 | 100·00 | |

The only analogues to this singular compound which I know, are those of urea and nitrate of silver, analysed by Werther*: the formulæ of which are:

$$C_2 H_4 N_2 O_2 + Ag NO_6$$

and

$$C_2 H_4 N_2 O_2 + 2 Ag NO_6.$$

These compounds, however, in consequence of the peculiar nature of urea, are not very stable, being decomposed when boiled with water into nitrate of ammonia and cyanate of silver. There likewise exists a compound of nitrate of silver and glycocoll, lately described by Horsford,† having the formula

$$C_4 H_4 NO_3 + Ag NO_6;$$

and, according to H. Rose, a compound of nitrate of silver with ammonia, 3 equivs. of this gas being absorbed by 1 equiv. of the former salt.

### PROTOCHLORIDE OF MERCURY AND CAFFEINE.

This beautiful compound is obtained when an aqueous or alcoholic solution of caffeine is added to a solution of protochloride of mercury; the latter being kept in excess, the fluid remains perfectly clear, but after the lapse of a few seconds, solidifies into a mass of very small crystals, which, when recrystallized from water or alcohol, and washed on a filter, are quite pure.

When pure, this salt is very similar in appearance to caffeine, the crystals not being, however, quite so large. It is very soluble in alcohol and water, hydrochloric, nitric, and oxalic acids, and seems to form with the latter a crystalline compound. It is nearly insoluble in ether. In reference to its constitution, it is distinguished from the double salt of platinum, for in this instance the caffeine is in direct combination with the chloride of mercury, and is exactly analogous to the corresponding compounds of leucoline and aniline investigated by Dr. Hofmann.‡ The mercurial compounds of this kind are generally easily decomposed; but the compound of chloride of mercury and caffeine is so stable, that it may be boiled in water for a considerable time without undergoing the slightest change in its properties. It may be dried at 100° C., and loses no weight at that temperature.

I endeavoured to combine the determination of the carbon, hydrogen, and mercury of this substance in *one* combustion, and have per-

* Liebig's Annalen, LVI, 262. † Ibid. LX, 36. ‡ Ibid. XIVII, 37.

fectly succeeded. The operation was conducted as follows:—The substance was mixed with chromate of lead and introduced into a combustion-tube of at least 26 inches in length. About 6 inches of copper turnings are placed above the mixture, leaving a space of 8 inches from the copper to the anterior end of the tube. A receptacle for the mercury is formed out of the tube itself, by contracting it about an inch from the copper turnings, and again so as to leave an elongated bulb of an inch in length. At the close of the operation, the tube is cut with a file at the posterior contraction. In order to separate the water from the mercury, the chloride of calcium tube (which has not been detached) is connected with an aspirator, and air admitted through chloride of calcium, the bulb being kept at a temperature of 100° C.

I obtained in my analysis the following numbers:

0·7833 grm. of substance gave:
0·5832 „ of carbonic acid,
0·1639 „ of water, and
0·3365 „ of mercury,

corresponding to the following per centage, which I place in comparison with the theoretical numbers:

| | | Theory. | | Experiment. |
|---|---|---|---|---|
| 16 equivs. | of Carbon . . | 96 | 20·68 | 2·030 |
| 10 „ | of Hydrogen . | 10 | 2·15 | 2·32 |
| 4 „ | of Nitrogen . . | 56 | 12·11 | — |
| 4 „ | of Oxygen . . | 32 | 6·89 | — |
| 2 „ | of Chlorine . . | 70 | 15·08 | — |
| 2 „ | of Mercury . . | 200 | 43·09 | 42·91 |
| 1 equiv. | of Mercury-salt | 464 | 100·00 | |

CAFFEINE AND TERCHLORIDE OF GOLD.

This compound is formed when a solution of terchloride of gold is added in excess to caffeine dissolved in dilute hydrochloric acid. If concentrated solutions are employed, the whole immediately solidifies into a mass of a most splendid lemon-yellow colour; this is to be washed with cold water and crystallized from alcohol, and finally dried in the water-bath.

The crystals from an alcoholic solution are in the form of long needles, of an orange-yellow colour, and a very bitter metallic taste; they are soluble in alcohol and water. When boiled in water for a short time, the salt is decomposed, a yellow flocculent matter precipitating, which is insoluble in alcohol, ether, and water, but soluble

in hydrochloric acid. If an aqueous solution is kept on the sand-bath for some hours at a temperature of about 68° C. it is also decomposed, and metallic gold separates in shining scales.

It is not altered when exposed to light, and when dry may be heated to 100° C. without undergoing decomposition.

When burnt with chromate of lead:

I. 0·8530 grm. of substance gave:
0·5525 „ of carbonic acid, and
0·1622 „ of water.
II. 0·3224 „ of substance gave:
0·1197 „ of gold.
III. 0·3019 „ of substance gave:
0·1115 „ of gold,

which give the following per centages:

| | I. | II. | III. |
|---|---|---|---|
| Carbon . . | 17·72 | — | — |
| Hydrogen . | 2·11 | — | — |
| Gold . . . | — | 37·12 | 36·93 |

corresponding to the formula:

$$C_{16}\,H_{10}\,N_4\,O_4,\,H\,Cl,\,Au\,Cl_3$$

as may be seen by the following table, in which the calculated and found quantities are placed in comparison:

| | Theory. | | Experiment. |
|---|---|---|---|
| 16 equivs. of Carbon . | 96·00 | 17·98 | 17·72 |
| 11 „ of Hydrogen . | 11·00 | 2·06 | 2·11 |
| 4 „ of Nitrogen . | 56·00 | 10·50 | — |
| 4 „ of Oxygen . | 32·00 | 6·01 | — |
| 4 „ of Chlorine . | 142·00 | 26·60 | — |
| 1 „ of Gold . . | 196·66 | 36·85 | 37·02 |
| 1 equiv. of Gold-salt . | 533·66 | 100·00 | |

The caffeine compounds which I have analysed, are therefore:

Caffeine . . . . . $C_{16}\,H_{10}\,N_4\,O_4$.
Platinum compound . $C_{16}\,H_{10}\,N_4\,O_4$, $HCl\,Pt\,Cl_2$.
Silver compound . . $C_{16}\,H_{10}\,N_4\,O_4$, $Ag\,NO_6$.
Mercury compound . $C_{16}\,H_{10}\,N_4\,O_4$, 2(Hg Cl).
Gold compound . . $C_{16}\,H_{10}\,N_4\,O_4$, HCl, $Au\,Cl_3$.

There exist several other double compounds of caffeine, which I have, however, not subjected to analysis.

On mixing a hot alcoholic solution of caffeine with an alcoholic solution of cyanide of mercury, beautiful needles of a double salt are deposited upon cooling, which correspond most likely to the mercury-salt I have just described. A solution of caffeine in hydrochloric acid gives a beautiful brown precipitate with protochloride of palladium; and the filtered solution deposits another compound in the form of yellow scales, very similar in appearance to iodide of lead.

Caffeine gives no precipitate with solutions of sulphate of copper, protochloride of tin, acetate of lead, and nitrate of suboxide of mercury. When boiled with sesquichloride of iron, a reddish-brown precipitate subsides upon cooling, which is perfectly soluble in water, and is most likely a double compound of caffeine and sesquichloride of iron.

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## XI.—*Researches on the Volatile Organic Bases.*

By Dr. A. W. Hofmann.

PROFESSOR AT THE ROYAL COLLEGE OF CHEMISTRY.

### I. ON THE ACTION OF CYANOGEN ON ANILINE, TOLUIDINE, AND CUMIDINE.

(Read before the Chemical Society of London, April 17, 1848.)

In a Memoir,* published some years ago, I described a series of chlorinated and brominated compounds, which stand in very intimate relation to aniline, although only part of them originate directly from that base. Independently of any special view respecting the constitution of these substances, we may consider them as aniline which has exchanged a certain amount of hydrogen for an equivalent quantity of chlorine or bromine. At a later period, in conjunction with Dr. Muspratt † I succeeded in preparing nitraniline, a compound which is derived from aniline in a similar manner; namely, by the exchange of hydrogen for the elements of hyponitric acid.

To complete these researches, the action of iodine and cyanogen upon aniline had still to be studied. An investigation of this kind appeared to be of some interest, more particularly as the imperfect knowledge we possess at present respecting the influence of these electro-negative radicals on organic bodies seemed to indicate a

* Liebig's Annalen, vol. LIII, p. 1. Memoirs of the Chemical Society, vol. II, p. 266.
† Ibid. vol. LVIII, p. 201. Ibid. vol. III, p. 111.

marked difference between their action and the effects which chlorine and bromine, so analogous in every other respect, produce under the same circumstances. A careful study of the action of cyanogen in particular, seemed to promise valuable results. We are already acquainted with a series of most remarkable organic cyanogen compounds, as cyanide of benzoyl and the cyanides of the alcohol radicals, which of late have been investigated with such beautiful results; all these compounds, however, have been produced by double decomposition of organic chlorides or sulphates with metallic cyanides; none of them have been obtained by the direct action of cyanogen. We possess at present no compound, the hydrogen of which, in conformity with the theory of substitution, is replaced by cyanogen, as we imagine it to be replaceable by chlorine, bromine, or the elements of hyponitric acid.

The experiments which I have described in the following pages relate only to the action of *cyanogen* on aniline and some of the analogous volatile alkalies, as toluidine and cumidine. The novelty of this reaction, as well as the great variety of metamorphoses arising from the compound nature of cyanogen, attracted my attention in the first instance, the behaviour of these substances with iodine being still under examination.

*Action of cyanogen on aniline.*—Cyanogen gas is absorbed by aniline, with the evolution of heat. After the colourless liquid has been exposed to the current for a few minutes, it assumes a yellow tint, which gradually darkens, until at last it becomes dark brown, and perfectly opaque. The odour of hydrocyanic acid, which was perceptible in the beginning of the process, is soon replaced by that of cyanogen. If the vessel containing the liquid is corked at this period, and left for twelve hours, the odour of cyanogen will have entirely disappeared; the liquid emits a powerful smell of prussic acid, and we find that a mass of crystals has been deposited. If instead of pure aniline, a cold alcoholic solution of this body is treated in the same manner, we observe exactly the same phenomena. The crystals deposited from the alcoholic solution are, however, purer and more perfect; the anhydrous base completely saturated with cyanogen gas solidifying to a dark mass, which it is difficult to purify.

Having ascertained the identity of the products resulting in both cases, I always preferred working with alcoholic solutions.

The crystals which have been deposited from the liquid, contain, especially if a great excess of cyanogen has been employed, a variety of substances, of which two are formed in considerable quantity.

If the action of the cyanogen has only been continued until the liquid smells strongly of it, the crystals are found to consist principally of *one* compound, with a variable but always slight admixture of another body. The composition of the new compound leads to the provisional name of *cyaniline*, which I shall make use of in the following pages.

*Preparation of cyaniline.*—The crystals of this body when separated from the solution are deeply coloured by the dark red mother-liquor which adheres to them. By repeated washing with cold alcohol, in which cyaniline is nearly insoluble, this colour may be almost entirely removed. It is, however, more economical, with regard both to time and alcohol, to dissolve the crystals (after separating the mother-liquor and washing once or twice with alcohol) in dilute sulphuric acid, when according to the duration of the action of the cyanogen, more or less of a reddish crystalline powder will remain behind. The sulphuric acid solution has a yellow tint, which is scarcely altered by treatment with animal charcoal. On the addition of caustic ammonia to this solution, a copious, slightly yellowish, floury precipitate is thrown down, evincing at once the basic nature of the new product. After separating the sulphate of ammonia, the base is still not perfectly pure; the yellowish colour does not belong to it. To remove the latter, the precipitate is dried and dissolved in a large amount of boiling alcohol, from which, at a temperature only a few degrees below the boiling-point, cyaniline separates in splendid iridescent crystalline plates. Sometimes, even after this treatment, the crystals are slightly coloured; one or two more crystallizations, however, yield them perfectly colourless. In operations of this kind, I found Plantamour's ebullition funnel very useful.

*Composition of cyaniline.*—The analysis of cyaniline afforded some difficulties, this body being very refractory and difficult of combustion. The formation of a crystalline film in the chloride of calcium tube could only be avoided by employing very long combustion tubes. This is the reason why the results of the first analyses of this body exhibit greater discrepancies than usually occur with the derivatives of aniline. Both hydrogen and carbon were found somewhat too high; the former on account of the sublimate, the latter in consequence of the formation of small quantities of binoxide of nitrogen. The later combustions were performed in very long tubes, the mixture having been made in the tube with a copper screw, to avoid increased attraction of moisture, and a long layer of copper turnings prevent-

ing the formation of binoxide of nitrogen. For every combustion, the substance was prepared by a special operation; in some cases protoxide of copper was used, in others chromate of lead.

I. 0·3938 grm. of cyaniline gave:
1·0219 „ „ carbonic acid, and
0·2300 „ „ water.
II. 0·2873 „ „ cyaniline gave:
0·7495 „ „ carbonic acid, and
0·1602 „ „ water.
III. 0·2608 „ „ cyaniline gave:
0·6700 „ „ carbonic acid, and
0·1415 „ „ water.
IV. 0·3272 „ „ cyaniline gave:
0·8417 „ „ carbonic acid, and
0·1860 „ „ water.
V. 0·2766 „ „ cyaniline gave:
0·7170 „ „ carbonic acid, and
0·1560 „ „ water.
VI. 0·3808 „ „ cyaniline gave:
0·9892 „ „ carbonic acid, and
0·2119 „ „ water.

These experimental numbers lead to the following per centage composition:

| | I. | II. | III. | IV. | V. | VI. |
|---|---|---|---|---|---|---|
| Carbon . . | 70·77 | 71·14 | 70·06 | 70·15 | 70·69 | 70·84 |
| Hydrogen . | 6·48 | 6·19 | 6·02 | 6·31 | 6·26 | 6·18 |

The amount of nitrogen, although known as the complement of the carbon and hydrogen, was, nevertheless, also directly determined. An analysis according to Dumas' method (but without the assistance of the air-pump), gave, as usual, a slight excess. A second determination was made by burning the base with soda-lime. In this operation, cyaniline, like all other aniline compounds, yields a large quantity of aniline, even when burnt in the longest tubes. In consequence of this behaviour, it appeared at the first glance impossible to ascertain the amount of nitrogen by means of this method. On some reflection, however, these difficulties appeared surmountable, provided the platinum-salt of aniline should prove quite as insoluble in a mixture of alcohol and ether as the corresponding ammonium compound. In both these platinum-salts the equivalents of nitrogen and platinum are in the same proportion. If it were possible, there-

fore, to obtain the *whole* amount of nitrogen of the substance in the form of an indefinite mixture of the two platinum-salts, this mixture would only require to be ignited in order to calculate the nitrogen from the platinum residue, in the usual manner. On experiment, I found that the platinum-salt of aniline is rather soluble in the usual mixture of alcohol and ether, but that it may be washed without loss with absolute ether, to which a few drops of alcohol have been added, in order to increase its solvent power for bichloride of platinum. A great number of analyses performed in this manner, have given perfectly satisfactory results.

VII. 0·4625 grm. of cyaniline, burnt in a current of carbonic acid gave:
98. c. c. of moist nitrogen at 21° C. and 0$^{m}$·7593 Bar.

VIII. 0·4485 grm. of cyaniline, burnt with soda-lime, gave:
0·7400 „ of platinum.

The per centage calculated from these numbers is:

| | VII. | VIII. |
|---|---|---|
| Nitrogen . . . . | 24·15 | 23·40 |

The simplest atomic expression for these results is the formula:

$$C_{14}\,H_7\,N_2 = Cy,\,C_{13}\,H_7\,N,$$

as may be seen from the following table:

| | Theory. | | Mean of the experiments. |
|---|---|---|---|
| 14 equivs. of Carbon . . . | 84 | 70·58 | 70·60 |
| 7 „ „ Hydrogen . . | 7 | 5·88 | 6·24 |
| 2 „ „ Nitrogen . . . | 28 | 23·54 | 23·77 |
| 1 equiv. of Cyaniline . . | 119 | 100·00 | 100·61 |

This formula is confirmed by the mode in which cyaniline is formed, by the decompositions which it undergoes, and by the analysis of several of its salts.

Three closely corresponding determinations, by means of platinum, led to the equivalent 119·28; a gold determination gave 118·54, results coinciding with the theoretical number.

When I first discovered this body, I was inclined to regard it as a product of substitution analogous to chloraniline and bromaniline, a view which appeared to be supported by the simultaneous production of hydrocyanic acid.

The formula:

$$C_{14} H_6 N_2$$

requires:

| | |
|---|---|
| Carbon | 71·18 |
| Hydrogen | 5·08 |
| Nitrogen | 23·74 |
| | 100·00 |

It is at once obvious, that the amount of hydrogen corresponding with this formula cannot be reconciled with the quantity found. Moreover, an accurate investigation of the new base soon proved this view to be erroneous. Cyaniline is formed by the direct union of one equivalent of aniline and one equivalent of cyanogen; the production of hydrocyanic acid belonging to a totally different reaction.

*Properties of cyaniline.*—When repeatedly crystallized from alcohol, cyaniline appears in small, thin crystalline plates, which possess a peculiar silver-like lustre, and are perfectly colourless, tasteless, and inodorous. The slight solubility of the substance prevents the formation of large and well-formed crystals. Ether, pyroxylic spirit, bisulphide of carbon, benzol, fatty and ethereal oils are not better solvents of cyaniline than alcohol. It is perfectly insoluble in water.

The new base is not volatile without decomposition. At a temperature of from 210° to 220° C. (442° to 450° F.) it fuses to a yellow oil, which, on cooling, solidifies with a crystalline structure. This fused mass is heavier than water, whilst the crystals float upon it. On heating the base a few degrees beyond its point of fusion, it is completely destroyed. The mass becomes brown, and is charred, with the evolution of aniline and cyanide of ammonium, the vapours of which mechanically carry off a small quantity of extremely minute crystals of cyaniline, which escape decomposition. The base cannot be volatilized with the assistance of aqueous vapour. Its solutions are perfectly neutral.

Cyaniline no longer exhibits the reactions which are peculiar to aniline, and in some measure to the chlorine and bromine compounds. The solution of the base imparts no yellow colour to fir-wood; hypochlorite of lime, and dilute solutions of chromic acid, are likewise without action upon it.

*Compounds of cyaniline.*—The preparation of the salts of cyaniline is attended with some difficulty. The base, when dissolved in acids, soon undergoes a series of metamorphoses, its cyanogen being transposed with the elements of water in a peculiar manner, whilst aniline

is reproduced. In order to avoid this decomposition, which I intend to describe to the Society in another paper, it is necessary to obtain the salts as fast as possible, in the solid form. This is the reason why those which are slightly soluble are most easily prepared.

The constitution of the salts of cyaniline is similar to that of the aniline salts. These compounds are, in fact, aniline salts, which have become associated with the elements of cyanogen. I have, however, vainly tried to obtain a salt of cyaniline by passing a current of cyanogen gas into an alcoholic solution of an aniline salt. Nitrate of aniline thus treated undergoes no change, whilst a solution of the hydrochlorate gives rise to the production of new compounds, which I shall describe at another opportunity.

*Hydrochlorate of cyaniline.*—The base is nearly insoluble in concentrated hydrochloric acid; it dissolves, however, readily in dilute acid, but it is impossible to obtain the hydrochlorate from this solution by concentration. The crystals which are deposited on evaporation are no longer a compound of cyaniline; they are usually a mixture of various products of decomposition, containing traces of cyaniline, if the solution has not been too dilute, and amongst which a substance invariably occurs possessing a most remarkable odour, and which is produced likewise so frequently during the various metamorphoses of aniline, that it can scarcely have escaped the notice of those who have worked with that base.

The hydrochlorate, however, may be easily prepared in the following manner. Cyaniline is dissolved in boiling, dilute, hydrochloric acid, the yellow solution is filtered and mixed, while still hot, with an equal volume of fuming hydrochloric acid, when the liquid again becomes colourless, and deposits, after a few minutes, an abundant quantity of white crystals. When washed once or twice with hydrochloric acid, and then with ether, these crystals are the pure hydrochlorate of cyaniline. This salt is extremely soluble in water and alcohol; it can be recrystallized from these liquids, but with considerable loss. The aqueous solution is distinguished by its sweet taste. It is so completely thrown down by fuming hydrochloric acid, that the filtrate no longer yields a precipitate with potassa. If the solution of this salt be mixed with an aqueous solution of aniline, cyaniline is at once set free, showing that the basic properties of aniline are weakened by its union with cyanogen. Hydrochlorate of cyaniline, when perfectly dry, may be preserved without change; in the presence of moisture, however, it undergoes a gradual decomposition, becoming insoluble in water, and being soon entirely converted into other products.

The analysis of this salt gave the following results:

I. 0·3043 grm. of salt, burnt with chromate of lead, yielded:
0·6028 „ „ carbonic acid, and
0·1495 „ „ water.
II. 0·1398 „ „ salt yielded:
0·1274 „ „ chloride of silver.
III. 0·3605 „ „ salt of a second preparation yielded:
0·3340 „ „ chloride of silver.
IV. 0·3005 „ „ salt of a third preparation yielded:
0·2787 „ „ chloride of silver.
V. 0·2687 „ „ salt yielded:
0·2480 „ „ chloride of silver.

These numbers correspond with the following per centage composition:

| | I. | II. | III. | IV. | V. |
|---|---|---|---|---|---|
| Carbon . . | 54·02 | — | — | — | — |
| Hydrogen . | 5·45 | — | — | — | — |
| Chlorine . . | — | 22·53 | 22·91 | 22·93 | 22·82 |

The formula:

$$Cy, C_{12} H_7 N, H Cl$$

requires the following numbers:

| | | Theory. | | Mean of experiments. |
|---|---|---|---|---|
| 14 equivs. of Carbon . . . | = | 84·0 | 54·01 | 54·02 |
| 8 „ „ Hydrogen . . | = | 8·0 | 5·14 | 5·45 |
| 2 „ „ Nitrogen . . . | = | 28·0 | 18·03 | — |
| 1 „ „ Chlorine . . . | = | 35·5 | 22·82 | 22·82 |
| 1 eq. of Hydrochlorate of Cyaniline | | 155·5 | 100·00 | |

*Hydrobromate of cyaniline.*—All the statements which I have made respecting the preparation and the properties of the hydrochlorate, are equally true of the hydrobromate. On the addition of the concentrated acid, it crystallizes even with more facility than the hydrochlorate. A carbon determination and an estimation of bromine gave the following numbers:

I. 0·3450 grm. of the salt, burnt with chromate of lead, gave:
0·5355 „ „ carbonic acid, and
0·1260 „ „ water.

II. 0·3448 grm. of the salt gave:
0·3220 „ „ bromide of silver.

The composition per cent is therefore:

| | I. | II. |
|---|---|---|
| Carbon . . . . . | 42.33 | — |
| Hydrogen . . . . | 4·05 | — |
| Bromine . . . . . | — | 39·25 |

The formula:

$$Cy, C_{12} H_7 N, H Br$$

requires the following numbers:

| | Theory. | | Experimental numbers. |
|---|---|---|---|
| 14 equivs. of Carbon . . . . . | 84·00 | 42·35 | 42·33 |
| 8 „ „ Hydrogen . . . . | 8·00 | 4·03 | 4·05 |
| 2 „ „ Nitrogen . . . . | 28·00 | 14·14 | — |
| 1 „ „ Bromine . . . . | 78·26 | 39·47 | 39·21 |
| 1 eq. of Hydrobromate of Cyaniline | 198·26 | 100·00 | |

*Hydriodate of cyaniline.*—This salt closely resembles the two former, but is soon decomposed by the action of the atmosphere, iodine being separated.

Of the compounds of cyaniline with the so-called oxygen acids, I have obtained only the nitrate in a fit state for analysis; this salt is difficultly soluble. Both the sulphate and oxalate are extremely soluble. Their solutions, when evaporated, are decomposed like the hydrochlorate.

*Nitrate of cyaniline.*—The base is easily soluble in boiling, dilute, nitric acid; on cooling, a beautiful nitrate crystallizes in long white needles, which may be recrystallized, from boiling water, without decomposition. This salt is only slightly soluble in cold water, and even less so in alcohol and ether. It contains equal equivalents of cyaniline and of the hydride of nitric acid. When burnt with oxide of copper, the following results were obtained:

I. 0·3244 grm. of the salt gave:
0·5504 „ „ carbonic acid, and
0·1415 „ „ water.
II. 0·5292 „ „ the salt gave:
0·9019 „ „ carbonic acid, and
0·2131 „ „ water,

which numbers correspond to the per centage composition:

| | I. | II. |
|---|---|---|
| Carbon . . . . . | 46·27 | 46·48 |
| Hydrogen . . . . | 4·80 | 4·47 |

leading to the formula:

$$Cy, C_{12} H_7 N, H NO_6.$$

as the following comparison with the theoretical numbers will show:

| | Theory. | | Mean of experiment. |
|---|---|---|---|
| 14 equivs. of Carbon . . . | 84 | 46·15 | 46·37 |
| 8 „ „ Hydrogen . . | 8 | 4·39 | 4·63 |
| 3 „ „ Nitrogen . . . | 42 | 23·07 | — |
| 6 „ „ Oxygen . . . | 48 | 26·39 | — |
| 1 equiv. of Nitrate of Cyaniline . . . . . | 182 | 100·00 | |

Nitrate of cyaniline forms a fine double salt with nitrate of silver.

*Platinum compound of cyaniline.*—A dilute solution of the hydrochlorate of cyaniline gives no precipitate with bichloride of platinum. On mixing, however, a boiling solution of the base in strong hydrochloric acid with a concentrated solution of bichloride of platinum, the double salt crystallizes on cooling, in beautiful orange-yellow needles, which become pure when washed with ether.

In the following determinations, different preparations of the salt were employed:

I. 0·3488 grm. of the platinum-salt, burnt with chromate of lead, gave:
0·3315 „ „ carbonic acid, and
0·0758 „ „ water.
II. 0·3386 „ „ the platinum-salt gave:
0·3220 „ „ carbonic acid, and
0·0790 „ „ water.
III. 0·4750 „ „ the salt being ignited left:
0·1436 „ „ platinum.
IV. 0·1125 „ „ the salt left:
0·0340 „ „ platinum.
V. 0·1540 „ „ the salt left:
0·0470 „ „ platinum.

Per centage composition:

| | I. | II. | III. | IV. | V. |
|---|---|---|---|---|---|
| Carbon . . . | 25·93 | 25·93 | — | — | — |
| Hydrogen . . | 2·41 | 2·59 | — | — | — |
| Platinum . . . | — | — | 30·23 | 30·22 | 30·51 |

The formula:

$$Cy, C_{12} H_7 N, H Cl, Pt Cl_2,$$

requires the following numbers:

| | Theory. | | Mean of experiment. |
|---|---|---|---|
| 14 equivs. of Carbon . . . | 84·00 | 25·83 | 25·93 |
| 8 „ „ Hydrogen . . | 8·00 | 2·46 | 2·50 |
| 2 „ „ Nitrogen . . | 28·00 | 8·61 | — |
| 3 „ „ Chlorine . . | 106·50 | 32·76 | — |
| 1 „ „ Platinum . . | 98·68 | 30·34 | 30·32 |
| 1 equiv. of Bichloride of Platinum and Cyaniline . | 325·18 | 100·00 | |

The solution of this double salt is decomposed with the same facility as the simple salts of cyaniline. It happened more than once that no crystals were deposited on cooling, too dilute a solution having been employed. On gently evaporating, the solution became turbid at a certain period, another salt in small crystals being separated, which was found to be the platinum-salt of aniline. On further concentration, brilliant octohedrons of the ammonium-salt appeared. In most cases a mixture of both salts was obtained, with various products of decomposition. I once succeeded in hitting the point of concentration when only the aniline-salt had formed. A specimen purified by washing with ether gave the following result:

0·2305 grm. of the platinum-salt gave:
0·0760 „ or 32·97 per cent of platinum.

The aniline-platinum compound contains 32·98 per cent. of platinum. In several other determinations, numbers were obtained which indicated a mixture of aniline and ammonia.

*Gold compound of cyaniline.*—This salt is obtained in the form of a yellow precipitate on adding a concentrated solution of terchloride of gold to an alcoholic or hydrochloric solution of cyaniline. In the latter case the solution should not contain too much free acid.

The analysis of a precipitate which had been washed with water and dried at 100° C. gave the following result:

0·2423 grm. of the gold-salt gave:
0·1040 „ or 42·92 per cent. of gold.

The formula

$$Cy, C_{12} H_7 N, H Cl, Au Cl_3$$

corresponds with the following values:

| | | Theory. | | Experiment. |
|---|---|---|---|---|
| 1 equiv. of Hydrochlorate of Cyaniline | | 155·50 | 33·92 | — |
| 3 „ of Chlorine . . . . . | | 106·50 | 23·21 | — |
| 1 „ of Gold . . . . . | | 196·66 | 42·87 | 42·92 |
| 1 „ of Gold-salt . . . . . | | 458·66 | 100·000 | |

The gold-salt of cyaniline is distinguished by its solubility in ether, a property belonging to various gold compounds with which I have lately become acquainted. The ethereal solution crystallizes on evaporation, but, in most cases the crystals are a mixture of the gold salts of cyaniline and aniline. The solution contains, besides, other products of decomposition. If the precipitate is dissolved in ether, when still moist, the salt is entirely decomposed, the crystals which are deposited consisting entirely of the pure aniline-salt, which is no longer soluble in ether. The analysis of these crystals gave the following results:

0·2385 grm. of gold-salt gave:
0·1080 „ or 45·28 per cent.

The theoretical per centage of gold in the aniline-gold salt is 45·45.

In the following table I subjoin the formulæ of the compounds analysed:

| | |
|---|---|
| Cyaniline . . . . . | Cy, $C_{12}$ $H_7$ N. |
| Hydrochlorate of Cyaniline | Cy, $C_{12}$ $H_7$ N, H Cl. |
| Hydrobromate of Cyaniline | Cy, $C_{12}$ $H_7$ N, H Br. |
| Nitrate of Cyaniline . . | Cy, $C_{12}$ $H_7$ N, H $NO_6$. |
| Platinum-salt . . . . . | Cy, $C_{12}$ $H_7$ N, H Cl, Pt $Cl_2$. |
| Gold-salt . . . . . | Cy, $C_{12}$ $H_7$ N, H Cl, Au $Cl_3$. |

I was curious to ascertain whether other bases were likewise capable of combining with cyanogen, in a manner similar to aniline. My attention was first directed to *ammonia*, which chemists are in the habit of considering as the type of the organic bases. I was quite unable, however, to obtain an ammonia compound analogous to cyaniline, although I brought the constituents into contact under various conditions; even in the anhydrous state.

*Toluidine* and *cumidine* were naturally the objects of the next experiments, which, as might have been expected, were more successful.

*Cyanotoluidine.*—On treating an alcoholic solution of toluidine* in

* The toluol which served for the preparation of toluidine had been obtained from light coal naphtha, in which, according to some recent investigations of Mr. Charles Mansfield, it is contained in considerable quantity.

the same manner with a current of cyanogen gas, the same phenomena take place which are observed with aniline. After a few hours, the red solution deposits a crystalline mass, from which the cyanotoluidine may be extracted with dilute hydrochloric acid. Potassa precipitates a white powder from this solution, which crystallizes from alcohol in small iridescent plates, in every respect resembling cyaniline. It is perhaps still less soluble in alcohol and ether than that base. I was satisfied with simply establishing the existence of this compound, which has evidently the composition:

$$C_{16}\,H_9\,N_2 = Cy,\ C_{14}\,H_9\,N.$$

*Cyanocumidine.*—The compound analogous to cyaniline is even more readily obtained from cumidine, the base which has recently been studied by Mr. Nicholson.*

An alcoholic solution of this body, when saturated with cyanogen, deposits, after a short time, long needles of the conjugate base. It is easily purified by repeated crystallization from boiling alcohol, in which it is far more soluble than cyaniline, so much so, indeed, that the cold alcoholic solution is densely precipitated by water, whilst that of cyaniline is merely rendered turbid.

The analysis of this substance gave the following results:

0·1308 grm. of cyanocumidine gave:
0·3565 „ „ carbonic acid, and
0·0980 „ „ water.

These numbers lead exactly to the formula:

$$C_{20}\,H_{13}\,N_2 = Cy,\ C_{16}\,H_{13}\,N,$$

as may be seen from the following table:

| | | Theory. | | Experiment. |
|---|---|---|---|---|
| 20 equivs. of Carbon . . . | 120 | 74·53 | 74·33 |
| 18 „ „ Hydrogen . . | 13 | 8·07 | 8·32 |
| 2 „ „ Nitrogen . . . | 28 | 17·40 | 17·35 |
| 1 equiv. of Cyanocumidine . | 161 | 100·00 | 100·00 |

I have also treated *nicotine* and *leucoline* with cyanogen gas. These two bases, however, although resembling aniline in a great many respects, seem nevertheless to belong to a perfectly different class of alkaloids. From nicotine and leucoline I vainly tried to produce the compounds corresponding to a large number of descendants which I derived by various processes from aniline, and whose

* Page 178.

analogues are easily obtained from toluidine and cumidine. Neither does cyanogen act on these latter bases as on aniline. The alcoholic solutions become brown, but neither crystals nor any basic products are deposited. I have not followed these changes quantitatively.

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The formation of the bases described in the preceding pages offers one of the first instances in which an organic alkali is found associated with another compound, the presence of which does not affect its saturating capacity. The existence of such compounds might have been anticipated; there was no assignable reason why, among the bases, a mode of combination should be wanting, which in so many cases has been recognized among the acids. Since Professor Liebig* first pointed out the constitution of formobenzoic acid, which both from its formation and decomposition he recognized as formic acid, associated with oil of bitter almonds—since that time up to the present moment, when in the hands of M. Dessaignes† we have seen hippuric acid splitting as it were into benzoic acid and glycocoll, so vast a number of analogous *conjugated organic acids* have been discovered, that this class of compounds may now be ranked amongst those which are best known.

*Conjugated organic bases* certainly exist in similar variety, and it is to be expected that the progress of science will soon add new members to the group we have just now become acquainted with. I may mention here that some researches on the action of chloride and bromide of cyanogen on aniline have elicited a new series of splendid alkaloids which evidently belong to the same class. In these substances, which I intend shortly to describe to the Society,‡ the basic atom of aniline is associated, not only with cyanogen, as in cyaniline, but with another very complicated compound in addition, the total weight of the adjunct considerably exceeding the equivalent of aniline.

The preceding investigation suggests a few remarks which I may offer here. Without entering at all upon the often-disputed question, whether the organic alkaloids are compounds of ammonia or amidogen, I cannot refrain from pointing out the influence which the formation of the new cyanogen bases is likely to exercise on some ideas which have of late been proposed, respecting the constitution of organic bases in general, the more so as those views seem to have emanated, partly at least, from my own researches.

* Liebig's Annalen, vol. x, p. 1. † Idem. vol. LIX, p. 149. ‡ Page 136.

Our notions of a relation between the amount of nitrogen in organic bases and their saturating capacity emanating from Liebig's earlier experiments on this subject, lost their signification with the discovery of alkaloids containing more than one equivalent of nitrogen. Liebig's own subsequent researches, *i.e.* his investigations of melamine, ameline and amelide,* left no doubt on this question; and since that period the class of similar bases has been considerably augmented. A relation between the nitrogen and the saturating capacity remained, nevertheless, extremely probable, and chemists now commenced to assume the nitrogen as existing in these bases under two different forms. In almost all cases, that portion of this element to which the basic properties were referred, was believed to be in the form of amidogen, ammonia, or oxide of ammonium, whilst the views respecting the other portion were for the most part less decided. Urea, e. g., was considered by some chemists to be anomalous cyanate of oxide of ammonium, whilst it appeared to others as the ammonia compound of a nitrogenous oxide—oxide of urén.

*Nitraniline*, which I have investigated in conjunction with Dr. Muspratt, likewise contains two equivalents of nitrogen, and there can be no doubt in this case respecting the difference of form in which this element is present. Independently of any particular view respecting the nature of aniline, it is evident that half of the nitrogen in nitraniline is present in the state of an oxide, as nitrous acid or as hyponitric acid; whilst the other half belongs to the original atom of aniline. Now, based on the composition of nitraniline, Fresenius† has founded a general view of the constitution of the organic bases. According to his opinion, all alkaloids, the equivalents of which contain more than one equivalent of nitrogen, are constituted similarly to nitraniline, they have to be considered as primitive bases, in which one or several equivalents of hydrogen are replaced by an equivalent amount of an oxide of nitrogen. The arbitrariness of this view is obvious;—what can entitle us to assume part of the nitrogen in an entire class of compounds as existing in this particular form, the occurrence of which, up to the present moment, has never been observed in vegetal productions? Among all the artificial bases, none are more dissimilar to the natural alkalies in most of their physical properties than the precise group to which nitraniline belongs. The preparation of cyaniline proves clearly that this additional nitrogen may exist just as well, and even with more probability, in the form of

* Liebig's Annalen, vol. xviii, p. 319. † Idem. vol. lviii, p. 322.

cyanogen. Fresenius considers strychnine, e. g., as an alkaloid containing hyponitric acid; with equal right, every other chemist might consider it as a cyanogen compound. Of the formulæ:

$$C_{44}\ H_{23}\ N_2\ O_4.$$
$$C_{44}\left\{\begin{matrix}H_{22}\\NO_4\end{matrix}\right\}N.$$
$$C_{42}\ H_{23}\ N\ O_4,\ C_2\ N$$

the first is certainly to be preferred, because it excludes every particular view of the constitution of this body, of which we are as yet entirely ignorant.

In a class of compounds so rich as that of the organic bases, a greater variety is certainly to be expected than is admissible on the theory of my friend, Dr. Fresenius. Possibly some of the natural bases may contain an oxide of nitrogen, possibly others may be cyanogen compounds; however, a great many other modes of constitution may yet be imagined, which present a similar degree of probability. The form in which nitrogen is contained in an alkaloid can only be ascertained by a careful study of its products of decomposition. The existence of cyanogen in cyaniline is evident from the mode of its formation, but even had this base been first extracted from a plant, its decompositions, which in this paper I have scarcely mentioned, would have stamped it at once as a cyanogen compound.

A detailed investigation of the metamorphoses of the natural bases is greatly hindered by the costliness of the materials, but there is scarcely a field in organic chemistry, the cultivation of which promises a richer harvest. The success which has attended the few experiments hitherto made in this direction, the production of leucoline from the bases of the quina bark, and the dissection of piperine into aniline and an organic acid, free from nitrogen, warrant the boldest expectations.

## XII.—*Researches on the Volatile Organic Bases.*

By Dr. A. W. Hofmann.

(Read before the Chemical Society of London, June 5, 1848).

### ON THE ACTION OF IODINE ON ANILINE.

The changes which organic bodies undergo when submitted to the action of bromine and of chlorine, have of late been examined with great care by various chemists; and it must be admitted, by every body who has followed these investigations with attention, that they have thrown much light on various parts of organic chemistry.

The metamorphoses produced by these two elements, so remarkable for their powerful affinities, are generally of so strongly marked a character, that, in the study of the derivatives thus obtained, the nature and constitution of a new body frequently unfold themselves in a most surprising manner. Chlorine and bromine have become in fact general agents in organic investigations. Their mode of action is known to us, based as it is, in most cases, upon their great affinity for hydrogen.

Less attention has hitherto been bestowed upon the action of iodine on organic bodies. The affinity of this element for hydrogen being much weaker, decompositions ensue with far greater difficulty.

Wöhler and Liebig, in their series of experiments on the radical of benzoic acid*—the first researches, perhaps, in which the influence of the saltformers on organic substances was investigated—found, that while part of the hydrogen in oil of bitter almonds could be eliminated with great facility by chlorine or by bromine, the corresponding iodine compound—iodide of benzoyle—could only be obtained indirectly, viz., by the action of chloride of benzoyle on iodide of potassium, iodine being dissolved with facility in oil of bitter almonds, but no decomposition taking place. In accordance with this observation, it was established by various subsequent researches, that many organic substances by themselves may be brought into contact with iodine without undergoing the slightest change, but that decomposition can be effected with the co-operation of alkalies. In these cases, the action is a common process of oxidation, an alkaline iodide being formed, while the organic body, under the influence of the liberated oxygen, is resolved into more simple compounds. The transformations of fusel oil, by means of iodine and potassa, into valerianic acid, of salicine into salicylous acid, of amygdaline into oil

* Liebig's Annalen, vol. III, p. 249.

of bitter almonds, are well-known instances of this mode of action. To these we may add the deportment of iodine with several of the volatile oils, such as oil of anise and fennel oil, which has only recently been investigated by Dr. Will.* Here, likewise, iodine exercises a feebly oxidizing action, substances richer in oxygen, but free from iodine being formed. In some cases, we also find the iodine combining with the newly-formed products; pyroxylic spirit, alcohol, citric acid, sugar, and several other substances, yield, as is well known, in this manner, iodoform along with various other products.

Moreover, we have a great variety of instances in which iodine is found to combine directly with organic bodies. Whether the blue compound of iodine and starch be a chemical combination or not, the entrance of iodine in this case is certainly not accompanied by an elimination of hydrogen; and we can scarcely adopt any other view respecting iodide of elayle, if we take into consideration the mode of formation of this body, and the facility with which it is again resolved into iodine and olefiant gas.

Analogous facts have been elicited with reference to the deportment of iodine with organic bases, which has been the subject of several investigations. Pelletier,† who first directed his attention to this question, arrived, by a series of experiments on strychnine, brucine, quinine, and cinchonine, at the conclusion that these bases were capable of combining directly in various proportions with iodine, an opinion which appeared to be confirmed by some subsequent experiments of Regnault.‡ The products thus obtained would correspond to the combinations of iodine with ammonia, described by Gay-Lussac, Bineau, and Millon. The analytical numbers given in Pelletier's investigation are, however, very unsatisfactory, and Regnault has paid but little attention to the subject.

The same question was again taken up by Bouchardat,§ according to whose experiments, the details of which, however, do not appear ever to have been published, these products should be considered as combinations of the hydriodates with iodine, whose representative in the ammonium series we find to be iodinated iodide of ammonium. It is possible that *both* classes of compounds exist: the subject requires further investigation.

If all the researches on the action of iodine on organic substances be glanced over, it will be found that there is scarcely a single instance

* Liebig's Annalen, vol. LXV, p. 230.

† Annales der Chimie et de Physique, 2ème sér. LXIII, p. 164. Liebig, Annalen, vol. XXII, p. 113.

‡ Liebig's Annalen, vol. XXIX, p. 58. § Comptes Rendus, t. IX, p. 475.

known, in which iodine does, like chlorine and bromine, eliminate and replace hydrogen, the fundamental properties of the compound remaining unaltered. These considerations gave rise to some experiments on the behaviour of iodine with aniline, which I wish to communicate to the Society in the following pages.

The action of chlorine and bromine on aniline, as is well known, is very powerful. By their agency, it appears that those products of substitution only can be obtained in which the whole of the replaceable hydrogen in the original aniline has been eliminated, and which have lost their basic properties. The anilines in which a smaller quantity of hydrogen is substituted, have, however, likewise been obtained by other processes, viz., by the action of alkalies on chlorinated and brominated isatine.*

The adoption of a similar method seemed to promise the preparation of iodinated aniline. Iodisatine, however, being as yet unknown, and considering the far less powerful affinity of iodine for hydrogen, I resolved to ascertain whether the desired object might not be accomplished by the direct treatment of aniline with iodine.

*Action of iodine on aniline.*—Iodine dissolves in anhydrous aniline, forming a dark brown liquid, and a rapid evolution of heat indicates at once a lively chemical reaction. If an excess of iodine has been avoided, long needles soon appear, surrounded by a brown mother-liquor. These crystals are exceedingly soluble in water and in alcohol, but less so in ether, by which liquid they may be separated from a great portion of the mother-liquor. Solution in water and ebullition with animal charcoal, and subsequent recrystallization, render them perfectly pure. The quantitative analysis proves them to be pure hydriodate of aniline.

This salt not having been previously analysed, an iodine determination was made,

0·2856 grm. of hydriodate of aniline gave:
0·3025 „ of iodide of silver.

The formula:

$$C_{12}\,H_7\,N,\,H\,I$$

requires:

| | Theory. | | Experiment. |
|---|---|---|---|
| 1 equiv. of Aniline . . . . . | 93·00 | 42·21 | — |
| 1 „ of Hydriodic acid . . . | 127·36 | 57·79 | 57·53 |
| 1 equiv. of Hydriodate of Aniline | 220·36 | 100·00 | |

* Memoirs of the Chemical Society, vol. II, p. 266.

The dark brown mother-liquor of this salt is a mixture of various substances: it contains, besides some hydriodate of aniline, a certain quantity of free iodine, which can be removed by alkalies, a brown product of decomposition, insoluble in acids and in alkalies, containing both aniline and iodine, and, lastly, the hydriodate of an iodinated base, to which, from its composition, the name of *iodaniline* belongs. The separation of the latter is easily effected by means of hydrochloric acid.

*Preparation of iodaniline.*—Anhydrous aniline is intimately mixed with one and a half times its weight of iodine. The brown liquid thus obtained solidifies after a very short time into a crystalline mass containing the above-mentioned substances, among which, however, iodaniline greatly preponderates. On the addition of common hydrochloric acid (sp. gr. 1·11) to this mass, the hydriodates are decomposed, difficultly soluble hydrochlorate of iodaniline remaining in the residue, while hydrochlorate of aniline enters into solution. Hydrochloric acid of greater strength should be avoided, as it would precipitate likewise some hydrochlorate of aniline. The salt, which is still much coloured, having been washed with hydrochloric acid for a short time, is now dissolved in boiling water: this solution deposits, on cooling, beautiful ruby-red, very distinct crystals of hydrochlorate of iodaniline, containing still a certain amount of free iodine. By repeated crystallizations from boiling water, these crystals become constantly paler, part of the free iodine remaining each time in solution. It is scarcely probable that these coloured crystals are combinations of hydrochlorate of iodaniline and iodine in chemical proportions. I have not, however, any experimental evidence to the contrary. Possibly some of Pelletier and Bouchardat's compounds may be of a similar kind. It is scarcely possible to remove entirely the free iodine, which adheres to them with great pertinacity by mere crystallization; it may be separated, however, with facility, by treatment with animal charcoal. By this process, not only the iodine, but also the brown product of decomposition, is nearly altogether removed. A colourless solution is obtained, which, filtered while hot, deposits, on cooling, a large quantity of iridescent plates of a hydrochlorate, very similar in appearance to benzoic acid.

On the addition of caustic ammonia to a solution of this salt, a beautifully white precipitate of iodaniline is obtained, which is, however, not yet absolutely pure; it is still contaminated with small quantities of a yellowish substance, containing iodine, (frequently also with traces of phosphate of lime from the charcoal), from which

it may, however, easily be separated by solution in alcohol, in which this yellow substance is quite insoluble. On mixing the alcoholic solution with water, a white crystalline mass of perfectly pure iodaniline is instantly thrown down; by evaporation on a water-bath, the base is separated in the form of yellow oily drops, which soon solidify to a crystalline mass.

The brown mother-liquor, filtered from the crude hydrochlorate of iodaniline, deposits, after a time, large crystalline plates, of an emerald-green colour, which possess the peculiar metallic lustre of the wing-covers of certain beetles. These crystals remain perfectly unaltered while in contact with the acid mother-liquor, but cannot be dried without undergoing change. The hydrochloric liquid being drained from them, they instantly become brown on exposure to the air. On the addition of water, the greater portion is rapidly dissolved, forming a light brown solution, on which a few oily drops still float. If this solution be boiled with animal charcoal, it becomes colourless, and deposits, on cooling, crystals of pure hydrochlorate of aniline, mixed perhaps with a small quantity of hydrochlorate of iodaniline.

I could not find a method of procuring the green crystals in a state fit for accurate analysis. In order to obtain an idea of their nature, some of the crystals were rapidly collected, purified and dried, as far as was practicable, by pressure between folds of bibulous paper, and kept *in vacuo* for a few days, when a small quantity of iodine was evolved. The solution of the substance thus prepared, was treated with hydrosulphuric acid, to convert the last trace of iodine into hydriodic acid, it was then boiled and thrown down with nitrate of silver. The precipitate was chloride of silver, mixed with traces only of iodide.

0·3200 grm. of the emerald crystals gave:
0·3323 „ „ silver-salt.

If the silver-salt had been pure chloride of silver, the crystals would contain 25·68 per cent of chlorine, the amount in hydrochlorate of aniline being 27·41 per cent.

From this approximative analysis, as well as from the general behaviour of the crystals, it is evident that they are, in fact, nothing but hydrochlorate of aniline, which has carried down a small quantity of iodine,* by which their beautiful appearance is produced.

* In an analysis of this kind, the determination by means of nitrate of silver should have yielded rather an excess of chlorine, the small quantity of iodine having been

Among the products of the action of iodine on aniline, I have mentioned several times a brown compound containing aniline and iodine, which is insoluble in acids and in alkalies. This substance is likewise insoluble in water. Alcohol and ether dissolve it; but it does not crystallize from any of these solutions; it is not volatile without decomposition. As nothing evinced the individuality of the substance, I did not investigate it any further.

*Composition of iodaniline.*—The analysis of iodaniline did not present any difficulties. Two determinations of carbon and hydrogen, with one estimation of iodine, were sufficient to establish the composition of the new body.

By burning the substance with protoxide of copper, the following results were obtained:

I. 0·4144 grm. of iodaniline gave:
0·5000 „ „ carbonic acid, and
0·1055 „ „ water.
II. 0·2149 „ „ iodaniline gave:
0·2621 „ „ carbonic acid, and
0·0553 „ „ water.
III. 0·4970 „ „ iodaniline converted into iodide of calcium by combustion with lime, and precipitated by nitrate of silver, gave:
0·5335 „ „ iodide of silver.

Per centage composition:

| | I. | II. | III. |
|---|---|---|---|
| Carbon . . . | 32·90 | 33·26 | — |
| Hydrogen . . | 2·82 | 2·85 | — |
| Iodine . . . . | — | — | 57·87 |

These numbers exactly represent the composition of moniodaniline,

$$C_{12}\left\{\begin{matrix}H_6\\I\end{matrix}\right\}N,$$

as the following comparison with the theoretical numbers will show:

| | Theory. | | Experiment. |
|---|---|---|---|
| 12 equiv. of Carbon . . . | 72·00 | 32·97 | 33·08 |
| 6 „ „ Hydrogen . . | 6·00 | 2·74 | 2·83 |
| 1 „ „ Iodine . . . | 126·36 | 57·86 | 57·87 |
| 1 „ „ Nitrogen . . | 14·00 | 6·43 | — |
| 1 equiv. of Iodaniline . . | 218·36 | 100·00 | |

calculated as chlorine. The presence, however, of a small amount of hydrochlorate of iodaniline (containing only 13·93 per cent. of chlorine), and the incompleteness of the method of desiccation, are sufficient to explain the small loss in the analysis.

The correctness of this formula was satisfactorily controlled by several determinations of the equivalent of the base as resulting from the analysis of its various salts.

Two determinations of platinum in the platinum-salt, which I shall mention hereafter, gave a mean per centage of 23·14 of platinum.

| | |
|---|---|
| Equivalent by experiment . . . | 220·26 |
| Equivalent by theory . . . . . | 218·36 |

The formation of iodaniline is effected by a simple process of substitution:

$$\underbrace{C_{12}\,H_7\,N}_{\text{Aniline.}} + 2\,I = \underbrace{C_{12}\left\{\begin{matrix}H_6\\I\end{matrix}\right\}N,\,HI.}_{\text{Hydriodate of Iodaniline.}}$$

*Properties of iodaniline.*—Iodaniline resembles aniline in most respects, and is even more similar to chloraniline and bromaniline. It is characterized by the same pleasant, somewhat vinous odour, the same aromatic and burning taste, the same solubility in alcohol, ether, pyroxylic spirit, acetone, bisulphide of carbon, and fatty and ethereal oils. In water it dissolves but very little. These solutions have not the slightest action on vegetal colours. Iodaniline is heavier than water.

When I first obtained this compound, I expected to see it crystallize in octohedrons, an anticipation which appeared to be supported by the crystalline form of chloraniline and bromaniline, and the generally assumed isomorphism of chlorine, bromine and iodine. But I have vainly searched the different crystallizations of iodaniline for octohedrons; from all the solutions which I tried, iodaniline was invariably deposited in prismatic crystals; from a boiling aqueous solution, it separates after some time in long hair-like needles. The crystalline mass obtained by the solidification of the fused base likewise exhibited no cleavage of an octohedron.

The crystals of iodaniline fuse far below the boiling-point of water into a yellow oil. A small quantity of this substance, heated in a water-bath, was completely fused at 60° C. (140° F.); at the moment of solidification the thermometer indicated 51° C. (124° F.) Sometimes the base remains liquid for a long period, even at common temperatures; it is then usually solidified at once by agitation. At higher temperatures iodaniline may be volatilized without much decomposition. With the assistance of aqueous vapour, it distils with the greatest facility. The vapour of the base burns with a brilliant smoky flame.

Like aniline and its chlorinated and brominated relatives, iodaniline imparts an intense yellow colour to fir-wood and the pith of the elder-tree; but it does not communicate the characteristic violet colour to hypochlorite of lime; a solution of this reagent on being mixed with iodaniline assuming only a slight red tint; nor is the aqueous solution altered by chromic acid. The dry and fused substance, however, when in contact with solid chromic acid, is destroyed with violence, but not inflamed like aniline and bromaniline.

*Compounds of iodaniline.*—The salts of iodaniline crystallize with the same facility as those of aniline. They are generally less soluble than the latter. By the entrance of iodine, the basic properties of aniline have been considerably weakened. A solution of aniline in water decomposes the salts of iodaniline with facility, and whilst aniline precipitates several metallic oxides, iodaniline is only capable of displacing alumina from its salts. The salts of oxide of zinc and sesquioxide of iron are not decomposed by iodaniline. With sulphate of copper a yellowish precipitate is produced, which is evidently a double salt.

*Hydrochlorate of iodaniline.*—This salt is but slightly soluble in cold water. The aqueous solution is precipitated nearly entirely by concentrated hydrochloric acid. From boiling water the salt crystallizes in plates or thin broad needles, which dissolve in alcohol, but are insoluble in ether.

Analysis gave the following results:

0·4531 grm. of hydrochlorate of iodaniline gave:
0·2573 „ „ chloride of silver.

The formula:

$$C_{12}\left\{\begin{matrix}H_6\\I\end{matrix}\right\}N, HCl,$$

requires the following numbers:

| | Theory. | | Experiment. |
|---|---|---|---|
| 1 equiv. of Iodaniline . . . . . | 218·36 | 85·69 | — |
| 1 „ „ Hydrochloric Acid . . | 36·50 | 14·31 | 14·44 |
| 1 eq. of Hydrochlorate of Iodaniline | 254·86 | 100·00 | |

*Hydrobromate of iodaniline.*—This salt resembles the preceding in every respect.

*Hydriodate of iodaniline* forms a radiated crystalline mass, far

more soluble than the preceding salts. It is very rapidly, decomposed.

*Sulphate of iodaniline*—This salt crystallizes in white brilliant scales. With respect to its solubility, it resembles the hydrochlorate precisely. The solution of this salt appears to be decomposed by ebullition; there remains, at least, a small quantity of a substance, which is completely insoluble in water.

Three determinations of sulphuric acid, in specimens of different preparations, gave a slight excess above the theoretical quantity.

I. 0·5249 grm. of sulphate of iodaniline gave:
0·2367 „ „ „ „ barium.
II. 0·3440 „ „ „ „ iodaniline gave:
0·2037 „ „ „ „ barium.
III. 0·3440 „ „ „ „ iodaniline gave:
0·1577 „ „ „ „ barium,

which quantities afford the following per centage:

| | I. | II. | III. |
|---|---|---|---|
| Hydride of sulphuric acid . . . . . | 18.94 | 19·56 | 19·24 |

The formula:

$$C_{12}\left\{\begin{matrix}H_6\\I\end{matrix}\right\}N, H\,SO_4,$$

requires,

| | Theory. | | Mean of experiments. |
|---|---|---|---|
| 1 equiv. of Iodaniline . . . . . | 218·36 | 81·68 | — |
| 1 „ „ Hydride of Sulphuric Acid | 49·00 | 18·32 | 19·24 |
| 1 equiv. of Sulphate of Iodaniline . | 267·36 | | |

*Oxalate of iodaniline.*—This salt forms splendid long, flattish needles, which, like the hydrochlorate, are difficultly soluble in water and in alcohol, and insoluble in ether.

The analysis of this salt gave the following results:

0·5020 grm. of oxalate of iodaniline gave:
0·0969 „ „ carbonate of lime.

The formula:

$$C_{12}\left\{\begin{matrix}H_6\\I\end{matrix}\right\}N, H\,C_2O_4,$$

requires the following numbers:

| | Theory. | | Experiment. |
|---|---|---|---|
| 1 equiv. of Iodaniline . . . . . | 218·36 | 82·92 | — |
| 1 „ „ Hydride of Oxalic Acid . | 45·00 | 17·08 | 17·37 |
| 1 equiv. of Oxalate of Iodaniline . | 263·36 | 100·00 | |

*Nitrate of iodaniline.*—This salt crystallizes from water in beautiful hair-like needles, often some inches in length. It is more soluble in water, especially when boiling, than any of the other salts I have examined. It is likewise easily soluble in alcohol and in ether. Its solution is notprecipitated by nitrate of silver.

*Bichloride of platinum and iodaniline.*—The hydrochlorate of the base yields a beautiful orange-yellow crystalline precipitate with bichloride of platinum, which may be easily purified by washing with ether.

The following are the experimental numbers obtained by analysis:

I. 0·2675 grm. of platinum-salt gave:
0·1650 „ „ carbonic acid, and
0·0451 „ „ water.
II. 0·2771 „ „ platinum-salt gave:
0·0643 „ „ platinum.
III. 0·1218 „ „ platinum-salt gave:
0·0281 „ „ platinum.

Per centage composition:

| | I. | II. | III. |
|---|---|---|---|
| Carbon . . . . | 16·82 | — | — |
| Hydrogen . . . | 1·87 | — | — |
| Platinum . . . | — | 23·20 | 23·07 |

corresponding exactly with the formula:

$$C_{12}\left\{\begin{matrix}H_6\\I\end{matrix}\right\}N,\ HCl,\ Pt\ Cl_2,$$

as may be seen from the following table:

| | Theory. | | Experiments. |
|---|---|---|---|
| 12 equiv. of Carbon . . . | 72·00 | 16·95 | 16.82 |
| 7 „ „ Hydrogen . . | 7·00 | 1·64 | 1·87 |
| 1 „ „ Nitrogen . . | 14·00 | 3·29 | — |
| 1 „ „ Iodine . . . | 126·36 | 29·79 | — |
| 3 „ „ Chlorine . . . | 106·50 | 25·09 | — |
| 1 „ „ Platinum . . | 98·68 | 23·24 | 23·14 |
| 1 equiv. of Platinum-salt . | 424·54 | 100.00 | |

A solution of hydrochlorate of iodaniline yields a scarlet precipitate with terchloride of gold, which is, however, rapidly decomposed.

The following table embraces the iodaniline compounds which have been analysed:

| | |
|---|---|
| Iodaniline . . . . . | $C_{12}\left\{\begin{matrix}H_6\\I\end{matrix}\right\}N$ |
| Hydrochlorate of iodaniline | $C_{12}\left\{\begin{matrix}H_6\\I\end{matrix}\right\}N$, H Cl |
| Sulphate of iodaniline . . | $C_{12}\left\{\begin{matrix}H_6\\I\end{matrix}\right\}N$, H $SO_4$ |
| Oxalate of iodaniline . . . | $C_{12}\left\{\begin{matrix}H_6\\I\end{matrix}\right\}N$, H $C_2O_4$ |
| Platinum-salt . . . . . | $C_{12}\left\{\begin{matrix}H_6\\I\end{matrix}\right\}N$, HCl, Pt $Cl_2$. |

*Products of decomposition of iodaniline.*—The metamorphoses which the iodinated base undergoes, when treated with various chemical agents, are very analogous to those of aniline; I have consequently studied them but cursorily.

Iodaniline, when gently heated with *potassium*, is decomposed with violence; iodide and cyanide of potassium being produced.

A concentrated aqueous, or alcoholic solution of *potassa* has no effect on iodaniline, not even at the boiling temperature.

*Chlorine* gives the same products with iodaniline, as with aniline itself; viz., trichloraniline and chlorophenisic acid. The iodine, in this case, is evolved in the form of chloride.

*Bromine* acts in a similar manner. On adding a few drops of bromine to an alcoholic solution of iodaniline, a crystalline mass is produced, which is pure tribromaniline, the whole of the iodine being evolved in the form of bromide.

In order to establish this fact, a bromine determination of the tribromaniline thus formed was made.

0·1200 grm. of substance, heated with lime, &c., gave:
0·2076 „ „ bromide of silver.

| | Theory. | Experiment. |
|---|---|---|
| Per centage of bromine in tribromaniline . . | 72·28 | 72·68 |

This result was to be expected. In inorganic chemistry, we always find iodine expelled by chlorine and bromine. And among organic substances, similar cases have also been observed. According to Bouchardat's experiments, iodoform is easily converted into chloroform or into bromoform, when acted on by chlorine or by bromine.

A mixture of *chlorate of potassa*, and *hydrochloric acid* convert iodaniline into chlorokinone (chloranil) and chlorophenisic acid.

Iodaniline is rapidly destroyed by boiling *nitric acid*. In this process the iodine is set free, and from the solution, scaly crystals of nitrophenisic acid are deposited on evaporation.

One peculiar decomposition I have still to mention.

Chemists are acquainted with the ingenious process which was devised by M. Melsens for substituting hydrogen in the place of chlorine in chloracetic acid. This acid, dissolved in water, is treated with a weak amalgam of potassium, and whilst the chlorine atoms are seized, as it were, by a portion of the potassium, the empty spaces become occupied by a corresponding number of atoms of hydrogen, liberated by the action of the same metal on the water. This process promises to become particularly important when employed in cases where the hydrogen term is still wanting. When Dr. Kolbe was in London, we made a few experiments of this kind together. Amongst other substances, we acted with amalgam of potassium on chloraniline and bromaniline, which, as was to be expected, are re-converted into aniline with the greatest facility. M. Melsens told me, that in performing the same experiments, he arrived at the same results.

Iodaniline I find likewise undergoes a similar change. The nitrate of this base, when brought into contact with amalgam of potassium, is at once decomposed, and the solution yields immediately a yellow precipitate with nitrate of silver. Only a small quantity, however, of aniline is reproduced in this process: the larger portion undergoes a further change, being converted into a yellow crystalline compound, of aromatic odour, the composition of which I have not yet ascertained.

The reproduction of aniline from iodaniline succeeds also with nascent hydrogen only. For effecting this, it is sufficient to heat an acid solution of sulphate of iodaniline, with some scraps of zinc, for a few minutes; starch paste indicates at once the liberation of iodine in the solution, while the addition of potassa, and agitation with ether, separates the aniline, which may now be detected by a solution of hypochlorite of lime.

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The action of *chlorine*, *bromine*, *iodine* and *cyanogen* on aniline, affords an interesting illustration of the decreasing affinities which these radicals manifest for hydrogen.

By treating aniline with *chlorine*, the molecular arrangement of

this body is nearly entirely destroyed; almost the whole is converted into chlorophenisic acid, a body only loosely connected with the original atom, while very small quantities of neutral trichloraniline are formed.

*Bromine* likewise acts very powerfully on aniline; yet its action is limited to a process of substitution, not less than three equivalents of hydrogen being replaced by bromine, in the formation of neutral tribromaniline.

With *iodine*, as we have seen, we may obtain a compound in which only one equivalent of hydrogen is replaced by iodine, the product retaining the basic properties of the original atom.

*Cyanogen*, finally, is no longer capable of eliminating hydrogen. It directly combines with aniline, producing a compound in which the original character of aniline has not been altered.

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## XIII.—*Researches on the Volatile Organic Bases.*

By Dr. A. W. Hofmann.

### III. ACTION OF CHLORIDE, BROMIDE, AND IODIDE OF CYANOGEN ON ANILINE.

#### MELANILINE, A NEW CONJUGATED ALKALOID.

(Read before the Chemical Society of London, June 14, 1847).

The original object of my experiments on the action of cyanogen upon aniline was the formation and the study of a cyanogen base, corresponding to chloraniline, bromaniline, iodaniline, and nitraniline.

These experiments, which I have lately communicated to the Society, have proved that the compound in question cannot be obtained in the manner indicated, but that the cyanogen combines directly with the aniline. The production of this body appeared, however, of sufficient interest to encourage me to apply some further methods promising a different result.

The idea naturally suggested itself to try the action of cyanogen associated with an element possessing an eminent affinity for hydrogen. There seemed to be a chance of thus eliminating hydrogen, the place of which would then be open for the cyanogen.

The gaseous chloride of cyanogen of Gay-Lussac, and Serullas' corresponding bromide, appeared to be compounds likely to produce the effect desired.

*Action of gaseous chloride of cyanogen on aniline.* — The gaseous chloride of cyanogen is obtained, as is well known, either by passing a current of chlorine into a solution of hydrocyanic acid, or by the action of this gas on moistened cyanide of mercury.

In the course of my experiments I have employed both methods, but as I soon found that the presence of water directly influenced the nature of the products arising from aniline, I have generally preferred the latter plan, which yields the chloride of cyanogen in a nearly dry state, and free from hydrochloric acid.

In treating aniline with chloride of cyanogen, it is necessary to avoid an admixture of free chlorine, which complicates the process, by simultaneously producing trichloraniline and chlorophenisic acid; it is important, therefore, to use a slight excess of cyanide of mercury, and not to begin the operation until the bottles previously filled with chlorine have become perfectly colourless.

In order to protect myself against the chloride of cyanogen, the odour of which for any length of time is insupportable, the gas was drawn, by means of a common aspirator, through the liquid to be saturated, the flask which contained the gas allowing the entrance of air through a narrow tube drawn out to a fine point. By means of this simple apparatus, the current of the chloride was easily regulated, and I was not exposed for a single moment to the influence of this annoying compound.*

On passing, in this manner, a current of chloride of cyanogen, prepared from cyanide of mercury, without further drying, into anhydrous aniline, chemical action is rendered at once perceptible by a rapid evolution of heat, the gas is absorbed with great avidity, the liquid assuming a brownish colour, and thickening gradually into a crystalline mass, the increasing consistency of which prevents the gas from passing freely. To complete the reaction, a gentle heat is now to be applied, sufficient to keep the compound in a state of fusion.

On cooling, the aniline is found converted into a solid transparent, slightly brownish, resinous substance, firmly adhering to the sides of the vessel. Towards the end of the operation, when the mass commences to become consistent, the absorption is exceedingly retarded, and the chloride of cyanogen passes into the aspirator. To avoid this loss, I have usually passed the gas through three wide test-tubes, half filled with aniline, and placed beside each other.

* On pouring aniline directly into the bottles filled with chloride of cyanogen, a double compound is obtained, composed of the product newly formed and the chloride of mercury from the preparation. The purification of the new compound becoming thus more difficult, I was induced to relinquish this mode of procedure.

The viscid mass chiefly consists of the hydrochlorate of a new organic base, which, for reasons to be detailed hereafter, I propose to call *Melaniline*. The hydrochlorate is always mixed with another body, the quantity of which varies with the amount of moisture contained in the chloride of cyanogen. The formation of this second substance, of which I shall speak at another opportunity, prevents the use of the solution of chloride of cyanogen, which is obtained by acting with chlorine upon an aqueous solution of hydrocyanic acid. On treating aniline with this solution, the chief product of the reaction is the second body above alluded to, whilst traces only of melaniline are formed.

*Preparation of melaniline.*—The crude product of the action of chloride of cyanogen on aniline, provided the treatment has been continued long enough, dissolves almost entirely in water, only a few brown drops remaining insoluble. The solution is considerably facilitated by boiling, and by the addition of a small quantity of hydrochloric acid. On adding ammonia, or better, a solution of potassa, to the filtered liquid, a white viscid mass is separated, which solidifies after a few moments into a hard crystalline compound. If the treatment with chloride of cyanogen has been incomplete, the solidification takes place only very gradually, the separated alkaloid being mixed with undecomposed aniline.

In order to purify the crude melaniline, the precipitate is freed from chloride of potassium by washing with cold water, and recrystallized once or twice from a mixture of equal volumes of alcohol and water. The boiling solution deposits the base, on cooling, in white plates of perfect purity.

*Composition of melaniline.*—The analysis of this base offered no difficulties, melaniline itself, as well as all its compounds, burning with great facility. The specimens of the base, its salts, and products of decomposition, were dried at 100° C.

When burnt with protoxide of copper, the following numbers were obtained:

I. 0·2414 grm. of melaniline gave:
0·6500 „ „ carbonic acid, and
0·1382 „ „ water.

II. 0·3423 „ „ melaniline gave:
0·9290 „ „ carbonic acid, and
0·2013 „ „ water.

III. 0·2258 „ „ melaniline gave:
0·6104 „ „ carbonic acid, and
0·1333 „ „ water.

IV. 0·2282 grm. of melaniline gave:
0·6180 „ „ carbonic acid, and
0·1277 „ „ water.

These numbers lead to the following per centage composition:

| | I. | II. | III. | IV. |
|---|---|---|---|---|
| Carbon . . . . . | 73·44 | 74·01 | 73·72 | 73·85 |
| Hydrogen . . . . . | 6·36 | 6·53 | 6·55 | 6·21 |

The nitrogen was determined according to the method of Bunsen; the following were the results obtaided:

| | | Corrected volume of the moist gas. | Temp. C. | Bar. |
|---|---|---|---|---|
| Level of mercury in the trough . . . . . | 260·0mm. | | | |
| Level of mercury in the tube | 118·0 „ | 116·7 | 13·6° | 733·7mm. |
| Height of mercury . . . | 142·0 „ | | | |
| Dry volume of gas reduced to 0°C. and 1000mm. bar. | =64·49 | | | |

After absorption of the carbonic acid:

| | | Corrected volume of dry nitrogen. | Temp. C. | Bar. |
|---|---|---|---|---|
| Level of mercury in the trough . . . . . | 261·0mm. | | | |
| Level of mercury in the tube | 16·4 „ | 14·2 | 13·3° | 735·4mm. |
| Height of mercury . . . | 244·6 „ | | | |
| Dry volume of nitrogen reduced to 0° C. and 1000 mm. bar. | =6·64 | | | |

Ratio of carbon equivalents, and nitrogen equivalents:

$$64{\cdot}49—6{\cdot}64 : 6{\cdot}64 = 100 : 11{\cdot}48.$$

Calculating from the mean per centage of carbon found (73·75), this ratio leads to 19·75 per cent. of nitrogen.

The above per centage composition, together with the analysis of various salts, lead to the following formula for melaniline:

$$C_{26}\,H_{13}\,N_3$$

as may be seen from the subjoined table.

| | Theory. | | Mean of experiments. |
|---|---|---|---|
| 26 equiv. of Carbon . . | 156 | 73·93 | 73·75 |
| 13 „ „ Hydrogen . . | 13 | 6·16 | 6·41 |
| 3 „ „ Nitrogen . . | 42 | 19·91 | 19·75 |
| 1 „ „ Melaniline . | 211 | 100·00 | 99·91 |

This formula was controlled by numerous determinations of the atomic weight.

The analysis of a well-crystallized double salt of platinum, gave as the mean of four nearly corresponding determinations, 23·48 per cent. of platinum. Five determinations of gold, in a similar double salt of gold, yielded 35·714 per cent. of gold.

| | |
|---|---|
| Equivalent deduced from the platinum-salt . . . | 214·02 |
| Equivalent deduced from the gold-salt . . . . | 211·04 |
| Mean . . . . . | 212·53 |
| Theoretical equivalent . . . . . | 211·00 |

A more perfect coincidence could not be expected.

The formula given above for melaniline explains the mode of formation of this new body in a most satisfactory manner. It is obvious, at the first glance, that melaniline is produced by the fusion of two aniline atoms, which have lost one equivalent of hydrogen in the form of hydrochloric acid, and have simultaneously assimilated a proportional amount of cyanogen.

$$\underbrace{2\,C_{12}\,H_7\,N}_{\text{Aniline.}} + \underbrace{C_2\,N\,Cl}_{\text{Chloride of Cyanogen.}} = \underbrace{C_{26}\,H_{13}\,N_3,\,H\,Cl.}_{\text{Hydrochlorate of Melaniline.}}$$

If the chloride of cyanogen is freed from the small quantity of moisture which it carries up from the bottles in which it has been prepared, by passing it through a chloride of calcium-tube, we find, indeed, that the whole mass of aniline is converted into hydrochlorate of melaniline, according to the above equation. The crystals which are deposited at the commencement of the reaction, are hydrochlorate of aniline, and these are gradually converted into the corresponding melaniline salt.

From the mode in which it is formed, the basic atom of melaniline may be regarded as an intimate combination of *aniline* with *cyanilide*, whence the rational formula of the new compound assumes the following shape:

$$\underbrace{C_{26}\,H_{13}\,N_3}_{\text{Melaniline.}} = \underbrace{C_{12}\,H_6\,N\,Cy}_{\text{Cyanilide.}},\ \underbrace{C_{12}\,H_7\,N}_{\text{Aniline.}}.$$

A corresponding ammonia-compound has not yet been observed but it is at once evident that there exists a certain analogy between this new body and *melamine* discovered by Professor Liebig. The latter alkaloid may be considered as a compound in which three equivalents of amide of cyanogen have been fused into one basic atom.

$$3\ \underbrace{(NH_2, C_2\,N)}_{\text{Amide of cyanogen.}} = \underbrace{C_6\,H_6\,N_6}_{\text{Melamine.}}.$$

An aniline base, exactly corresponding to melamine, would have the composition:

$$C_{42}\,H_{18}\,N_6,$$

as will be apparent from the following equation:

$$3\ (C_{12}\,H_6\,N,\ C_2\,N) = C_{42}\,H_{18}\,N_6.$$

In the new compound we have a third of the true aniline-melamine, associated with an additional equivalent of aniline:

$$\frac{C_{42}\,H_{18}\,N_6}{3} + C_{12}\,H_7\,N = C_{26}\,H_{13}\,N_3;$$

a conjugated base is thus formed, which likewise saturates only *one* equivalent of acid.

The name *melaniline*, which I have adopted, should, therefore, be regarded as a convenient, but provisional term, in place of which another more rational one must be substituted, as soon as our views respecting the mode of combination of the elements in this compound have gained a more positive foundation.

*Properties of melaniline.*—This base, when pure, crystallizes in white, hard, pulverizable plates, which, if exposed to the air while damp, readily assume a slight red tinge.

The crystals are quite devoid of smell; they have, however, a bitter taste (particularly when in alcoholic solution) which remains for some time on the palate. They fuse at about 120°—130° C. to a slightly coloured oil, which, on cooling, solidifies with a crystalline texture; if, however, the temperature is raised to 140° or 150° C., decomposition ensues, colourless aniline distils over, and a transparent light brown amorphous mass remains in the retort. I shall return to this remarkable decomposition at another opportunity. The crystals of melaniline float on the surface of water; but, when fused, the base sinks to the bottom.

Melaniline is only slightly soluble in cold water; a somewhat larger quantity is dissolved by boiling water, from which, on cooling, it crystallizes in small plates. Alcohol and ether dissolve the base with facility, as do likewise the hydrated oxide of methyle, acetone, bisulphide of carbon, and fatty and ethereal oils. Melaniline crystallizes best from a boiling mixture of water and alcohol, in which the latter predominates; on allowing the solution to cool gradually, the base is deposited in long white needles. Melaniline has scarcely any action on vegetal colours; turmeric paper is not changed in the least by it, and only the most delicately reddened litmus paper is tinged slightly blue. The solutions of the salts of melaniline do not colour firwood; chromic acid does not effect that peculiar change which it occasions in aniline salts. A solution of melaniline may be heated to ebullition with dilute chromic acid without a reduction of the acid occurring (only on continued boiling, the base is gradually attacked and resolved into other compounds); nor does a solution of hypochlorite of lime produce the violet colour characteristic of aniline.

An aqueous solution of melaniline, in consequence of the slight solubility of this base in water, affords precipitates with very few reagents. Salts of oxide and sesquioxide of iron are not precipitated; solution of sulphate of zinc is rendered slightly turbid; sulphate of copper, nitrate of silver, and protochloride of mercury, produce flocculent precipitates, which are double compounds of the base. Of these I have investigated only the silver precipitate. Bichloride of platinum and terchloride of gold produce beautiful double compounds with the hydrochlorate, to which I shall recur hereafter.

*Combinations of melaniline.*—The base dissolves easily in all acids, with a slight evolution of heat, and forms with most of them nicely crystallizable, colourless or slightly reddish salts, which are capable of double decomposition.

The neutral salts of melaniline have no action on reddened litmus paper. They are exactly analogous in their constitution to the salts of ammonia. Their solutions, all of which possess an intensely bitter taste, are decomposed by ammonia, and more perfectly by potassa or soda, the melaniline being separated as a dazzling white precipitate, which becomes crystalline almost immediately. The carbonates of the alkalies likewise precipitate the base, with evolution of carbonic acid.

With respect to its basic properties, melaniline is nearly allied to aniline; an aniline salt cannot be decomposed by melaniline, nor has aniline any action on the salts of the other base.

I have submitted several salts of melaniline to a closer examination,

in order to obtain further proof of the correctness of the formula given above.

*Sulphate of melaniline.*—This salt crystallizes a short time after the solutions are mixed, in rhombic plates, which aggregate into star-like groups. The crystals are somewhat difficultly soluble in cold, more easily in boiling water. They likewise dissolve in alcohol and ether.

A determination of the sulphuric acid gave the following results:

0·3585 grm. of sulphate of melaniline, dried at 100° C. gave:
0·1572 „ „ sulphate of barium, corresponding to 18·42 per cent. of hydrided sulphuric acid.

Hence, the salt is a neutral sulphate, having the formula,

$$C_{26}\,H_{13}\,N_3,\,H\,SO_4.$$

| | | Theory. | Experiment. |
|---|---|---|---|
| 1 equiv. of Melaniline . . . . . | 211 | 81·16 | — |
| 1 „ „ Hydrided Sulphuric Acid | 49 | 18·84 | 18·42 |
| 1 equiv. of Sulphate of Melaniline . | 260 | 100·00 | |

*Nitrate of melaniline.*—This compound is that which of all the salts of melaniline crystallizes with the greatest ease; it separates from a boiling aqueous solution on cooling, in needles, and indeed, so completely, that the mother-liquor gives but a very faint precipitate with ammonia or potassa. I was thus frequently enabled, during the progress of this investigation, to apply nitric acid as a reagent for melaniline.

This salt is soluble in alcohol, but scarcely so in ether; it is stable in atmospheric air, but very soon acquires a red tint.

The analysis of this salt led to the formula:

$$C_{26}\,H_{13}\,N_3,\,H\,NO_6.$$

When burnt with oxide of copper, the following numbers were obtained:

0·2831 grm. of nitrate of melaniline gave:
0·5872 „ „ carbonic acid, and
0·1318 „ „ water.

| | | Theory. | Experiment. |
|---|---|---|---|
| 26 equiv. of Carbon . . . . . | 156 | 56·93 | 56·57 |
| 14 „ „ Hydrogen . . . . | 14 | 5·10 | 5·17 |
| 4 „ „ Nitrogen . . . . | 56 | 20·43 | — |
| 6 „ „ Oxygen . . . . . | 48 | 17·54 | — |
| 1 equiv. of Nitrate of Melaniline . | 274 | 100·00 | |

*Binoxalate of melaniline.*—This compound is exactly similar in outward appearance to the sulphate; it crystallizes when the base is supersaturated with oxalic acid. The crystals are difficultly soluble in water and in alcohol, when cold, but easily at the boiling temperature. They are nearly insoluble in ether. The salt, when heated, evolves equal volumes of carbonic oxide and carbonic acid, and aniline distils over, accompanied by the same pungent body which I had occasion to mention in my description of cyaniline. At the close of the operation, the neck of the retort becomes coated with long white needles, and a transparent residue remains, similar to that obtained on heating melaniline. The analyses of this salt show it to be a binoxalate, as is indicated by its acid reaction.

I. 0·5560 grm. of binoxalate of melaniline, precipitated with ammonia and chloride of calcium, &c., yielded :
0·1840 „ „ carbonate of lime.
II. 0·4910 „ „ the salt gave :
1·0866 „ „ carbonic acid, and
0·2302 „ „ water.

The formula,

$$C_{26}\,H_{13}\,N_3,\ H\,C_2O_4,\ H\,C_2O_4,$$

requires the following numbers :

| | Theory. | | Experiment I. |
|---|---|---|---|
| 1 equiv. of Melaniline . . . . | 211 | 70·10 | — |
| 2 „ „ Hydrided Oxalic Acid | 90 | 29·90 | 29·73 |
| 1 eq. of Binoxalate of Melaniline | 301 | 100·00 | |

| | Theory. | | Experiment II. |
|---|---|---|---|
| 30 equiv. of Carbon . . . . | 180 | 59·80 | 60·35 |
| 15 „ „ Hydrogen . . . . | 15 | 4·98 | 5·20 |
| 3 „ „ Nitrogen . . . . | 42 | 13·95 | — |
| 8 „ „ Oxygen . . . . | 64 | 21·27 | — |
| 1 eq. of Binoxalate of Melaniline | 301 | 100·00 | |

*Phosphate of melaniline.*—This salt is very soluble, and crystallizes slowly. I have not analysed it.

*Hydrochlorate of melaniline.*—This is the most soluble of all the melaniline salts. The solution of the base in hydrochloric acid does not crystallize by spontaneous evaporation in the open air. When kept over sulphuric acid, or in a water-bath, it dries up to a slightly coloured gummy mass, which only becomes crystalline very gradually.

It is hence difficult to obtain this salt in a fit state for analysis. I endeavoured to determine its composition, by ascertaining the increase of weight produced by dissolving the base in hydrochloric acid, and desiccating. It appears, however, that the whole excess of acid cannot be removed in this manner. I obtained, in one experiment of this kind, 16 per cent. of hydrochloric acid, instead of 14·74 per cent., which would correspond to the formula:

$$C_{26}\,H_{13}\,N_3,\,HCl.$$

*Hydrobromate of melaniline.*—This salt is likewise very soluble, less so, however, than the hydrochlorate, and may be obtained without difficulty in fine stellated tufts of needles. It is, like the corresponding cyaniline salt, less soluble in concentrated hydrobromic acid than in water.

Its analysis led to the formula:

$$C_{26}\,H_{13}\,N_3,\,HBr.$$

0·3494 grm. of hydrobromate of melaniline gave:
0·2252 „ „ bromide of silver.

| | Theory. | | Experiment. |
|---|---|---|---|
| 1 equiv. of Melaniline. . . . . | 211·00 | 72·70 | — |
| 1 „ „ Hydrobromic Acid . . | 79·26 | 27·30 | 27·42 |
| 1 eq. of Hydrobromate of Melaniline | 290·26 | 100·00 | |

*Hydriodate of melaniline.*—A concentrated solution of hydriodic acid converts the base into a yellow oil, which falls to the bottom of the vessel, and solidifies after a time to a crystalline mass. This is soluble in boiling water, being again separated on cooling, in oily drops, which only gradually solidify. It is likewise soluble in alcohol. When in contact with air, it is rapidly decomposed, the hydriodic acid undergoing decomposition with separation of iodine.

The specimen employed in the following analysis had been superficially decomposed; hence the slight loss of iodine.

0·6727 grm. of hydriodate of melaniline gave:
0·4575 „ „ iodide of silver.

The formula:

$$C_{26}\,H_{13}\,N_3,\,HI,$$

requires:

| | Theory. | | Experiment. |
|---|---|---|---|
| 1 equiv. of Melaniline . . . . . | 211·00 | 62·36 | — |
| 1 „ „ Hydriodic Acid . . . . | 127·36 | 37·64 | 36·96 |
| 1 equiv. of Hydriodate of Melaniline . | 338·36 | 100·00 | |

*Hydrofluate of melaniline.*—This salt is easily formed by dissolving melaniline in dilute hydrofluoric acid. It may be obtained in well-formed crystals, which, however, possess always a reddish tint. It is pretty soluble in water, less so in alcohol.

*Bichloride of platinum and melaniline.*—Bichloride of platinum produces, in a solution of the hydrochlorate, a slightly crystalline, pale yellow precipitate. The filtrate deposits, after a time, regular orange-yellow crystals. These, and the precipitate, have the same composition.

This platinum-salt is slightly soluble in boiling water, the yellow crystals being also deposited on cooling. It is less soluble in alcohol, and insoluble in ether.

The analysis of specimens of different preparations, gave the following results:

I. 0·5585 grm. of platinum-salt, burnt with chromate of lead, gave:
0·7621 „ „ carbonic acid, and
0·1836 „ „ water.

II. 0·6875 „ „ platinum-salt, ignited with lime, dissolved in nitric acid and precipitated with nitrate of silver, gave:
0·7085 „ „ chloride of silver.

III. 0·3707 „ „ platinum-salt yielded:
0·0871 „ „ platinum.

IV. 0·5030 „ „ platinum-salt yielded:
0·1187 „ „ platinum.

V. 0·2670 „ „ platinum-salt yielded:
0·0623 „ „ platinum.

The following determination was made with the crystallized salt:

VI. 0·3697 grm. of platinum-salt yielded:
0·087 „ „ platinum.

From these numbers, the following per centage composition is deduced:

| | I. | II. | III. | IV. | V. | VI. |
|---|---|---|---|---|---|---|
| Carbon . . | 37·21 | — | — | — | — | — |
| Hydrogen . | 3·65 | — | — | — | — | — |
| Chlorine . | — | 25·49 | — | — | — | — |
| Platinum . | — | — | 23·49 | 23·59 | 23·33 | 23·53 |

The formula:

$$C_{26}\,H_{13}\,N_3,\,HCl,\,Pt\,Cl_2,$$

requires the following numbers:

| | Theory. | | Mean of experiment. |
|---|---|---|---|
| 26 equiv. of Carbon . . . . | 156·00 | 37·39 | 37·21 |
| 14 „ „ Hydrogen . . . | 14·00 | 3·35 | 3·65 |
| 3 „ „ Nitrogen . . . | 42·00 | 10·09 | — |
| 3 „ „ Chlorine . . . . | 106·50 | 25·52 | 25·49 |
| 1 „ „ Platinum . . . | 98·68 | 23·65 | 23·48 |
| 1 equiv. of Platinum-salt . . | 417·18 | 100·00 | |

*Terchloride of gold and melaniline.*—On mixing a moderately concentrated solution of hydrochlorate of melaniline with terchloride of gold, the liquid immediately assumes a deep yellow colour, becoming turbid and opaque. In about half an hour, it again becomes clear, and is now filled with splendid gold-coloured needles. If the solution of the hydrochlorate is concentrated, terchloride of gold produces an abundant yellow precipitate. The salt is difficultly soluble in water, but more easily in alcohol, and is exceedingly soluble in ether. If the precipitate suspended in water is shaken with ether, a deep yellow ethereal solution of the salt is obtained floating on the colourless liquid. If this solution is allowed to evaporate spontaneously, it sinks to the bottom of the water, at a certain state of concentration, in the form of oily drops of a ruby colour, which solidify, after a time, in the form of beautiful four-sided prisms.

Its analysis gave the following numbers:

I. 0·6791 grm. of gold-salt gave:
0·7125 „ „ carbonic acid, and
0·1635 „ „ water.
II. 0·2150 „ „ gold-salt gave:
0·0765 „ „ gold.
III. 0·8259 „ „ gold-salt gave:
0·2956 „ „ gold.

In the analyses II. and III. the salt was employed in the precipi-

tated state; for the following determinations, the salt had been crystallized from ether:

IV. 0·2785 grm. of gold-salt gave:
0·0995 „ „ gold.
V. 0·3374 „ „ gold-salt gave:
0·1207 „ „ gold.
VI. 0·3663 „ „ gold-salt, gave:
0·1309 „ „ gold.

From these numbers, the following per centage composition is deduced:

| | I. | II. | III. | IV. | V. | VI. |
|---|---|---|---|---|---|---|
| Carbon . . . | 28·61 | — | — | — | — | — |
| Hydrogen . . | 2·67 | — | — | — | — | — |
| Gold . . . . | — | 35·58 | 35·79 | 35·72 | 35·77 | 35·73 |

which lead to the formula:

$$C_{26}\,H_{13}\,N_3,\,H\,Cl,\,Au\,Cl_3,$$

as may be seen from the subjoined table:

| | Theory. | | Experiment. |
|---|---|---|---|
| 26 equiv. of Carbon . . . | 156·00 | 28·32 | 28·61 |
| 14 „ „ Hydrogen . . | 14·00 | 2·54 | 2·67 |
| 3 „ „ Nitrogen . . . | 42·00 | 7·62 | — |
| 4 „ „ Chlorine . . . | 142·00 | 25.81 | — |
| 1 „ „ Gold . . . . | 196·66 | 35·71 | 35·71 |
| 1 equiv. of Gold-salt . . . | 550·66 | 100·00 | |

*Nitrate of silver and melaniline.*—An alcoholic solution of melaniline produces, with nitrate of silver, a white precipitate, which adheres firmly to the sides of the vessel in the form of a resinous matter. I collected this mass with a glass rod, and reduced it to a fine powder with alcohol, to remove any excess of melaniline; it was then washed with alcohol (I). On endeavouring to crystallize a portion from alcohol, it was decomposed with the separation of metallic silver. The same compound may be obtained in hard, rounded crystals, on mixing alcoholic solutions of melaniline and nitrate of silver. The liquid remains clear for some hours, it then slowly deposits the compound (II).

Both preparations burnt with the greatest difficulty.

I. 0·2492 grm. of silver-salt gave:
0·0430 „ „ metallic silver.

II. 0.3200 „ „ silver-salt gave:
0·0570 „ „ metallic silver,

which correspond to the following per centage composition:

| | I. | II. |
|---|---|---|
| Silver . . . . | 17·41 | 17·81 |

The amount of silver found, corresponds approximately to the formula:

$$2\,(C_{26}\,H_{13}\,N_3),\,Ag\,NO_6.$$

| | | Theory. | | Mean of experiments. |
|---|---|---|---|---|
| 2 equiv. | of Melaniline . . . . . | 422 | 72·28 | — |
| 1 „ | „ Silver . . . . . | 108 | 18·24 | 17·61 |
| 1 „ | „ Anhydride of Nitric Acid | 62 | 10·47 | — |
| 1 equiv. | of Silver-salt . . . . . | 592 | 100·47 | |

I have not had time to confirm this somewhat uncommon composition by further experiments.

Chloride of mercury gives a white precipitate, in solutions of melaniline, which is easily soluble in a few drops of hydrochloric acid. By spontaneous evaporation, this solution deposits long white needles.

*Metamorphoses of melaniline.*—The following pages contain a few observations respecting the transformations of melaniline when exposed to the action of various agents. These transformations, however, present so great a diversity, the descendants of melaniline ramify in so many directions, that these remarks must only be considered as a first contribution towards this part of the history of our compound. As soon as I find leisure, I hope to return to this subject.

*Action of chlorine on melaniline—Dichloromelaniline*—From the complete transformation of aniline, when under the influence of chlorine, a still more decided action might have been expected in the case of melaniline, this body being evidently a compound of a higher order. It appeared not improbable that this reaction might throw some light upon the real manner in which the elements are combined in melaniline. This expectation has remained as yet unfulfilled, the action of chlorine, as far, at least, as I have studied it, assuming merely the form of a simple process of substitution.

If a solution of hydrochlorate of melaniline is mixed with a large excess of chlorine water, the whole of the base is separated in the form of a resinous mass, which becomes hard after a time, but shews

no signs of crystallization. The filtrate is no longer precipitated by potassa. The resinous body is insoluble in water, but soluble in alcohol; it possesses neither basic nor acid properties. I have not analysed it, but its general deportment characterizes it as a substitution-product, bearing a relation to melaniline, similar to that which trichloraniline bears to aniline.

On adding chlorine water, gradually and in small quantities, to a solution of hydrochlorate of melaniline, the liquid becomes turbid after each addition, but is rendered immediately clear by agitation. The point may be easily attained when the resinous mass, that separates, no longer dissolves on agitation. If the solution is now filtered and evaporated till a pellicle forms, it deposits, on cooling, stellated groups of white needles. If the evaporation has been carried too far, a yellowish oil separates, which becomes solid and exhibits a crystalline texture.

These crystals are the hydrochlorate of a chlorinated base, which I propose to call *dichloromelaniline*. They are easily soluble in ether, and tolerably so in alcohol, but dissolve with difficulty in water. Ammonia precipitates the base from the hydrochloric solution as a dazzling white flocculent substance, crystallizing from alcohol in hard plates. I have not analyzed either the hydrochlorate, or the base, as I have carefully investigated the analogous bromine compounds.

The analysis of the platinum-salt, however, which I subjoin, proves undoubtedly, that the body in question is dichloromelaniline:

$$C_{26}\left\{\begin{matrix}H_{11}\\Cl_2\end{matrix}\right\}N_3.$$

*Bichloride of platinum and dichloromelaniline.*—The solution of the hydrochlorate gives, with bichloride of platinum, a fine orange-yellow precipitate, which is easily purified by washing with ether. The analysis of this compound gave the following results:

| | | | |
|---|---|---|---|
| 0·3435 | grm. | of | platinum-salt, when burnt with chromate of lead, gave: |
| 0·4039 | „ | „ | carbonic acid, and |
| 0·0785 | „ | „ | water. |
| 0·1976 | „ | „ | platinum-salt, yielded: |
| 0·0400 | „ | „ | platinum. |

The per centage composition deduced from these experiments leads to the formula:

$$C_{26}\left\{\begin{matrix}H_{11}\\Cl_2\end{matrix}\right\}N_3,\ H\,Cl,\ Pt\,Cl_2,$$

as may be seen from the following table:

| | | Theory. | | Experiment. |
|---|---|---|---|---|
| 26 equiv. of Carbon . . . . . | 156·00 | 32·08 | 32·06 |
| 12 „ „ Hydrogen . . . . | 12·00 | 2·46 | 2·54 |
| 3 „ „ Nitrogen . . . . | 42·00 | 8·63 | — |
| 5 „ „ Chlorine . . . . | 177·50 | 36·54 | — |
| 1 „ „ Platinum . . . . | 98·68 | 20·29 | 20·24 |
| 1 equiv. of Bichloride of Platinum and Dichloromelaniline . . | 486·18 | 100·00 | |

*Action of bromine on melaniline.*—The phenomena observed on treating a solution of the hydrochlorate of melaniline with bromine are very similar to those obtained with chlorine. The white crystals obtained on evaporating the solution are the hydrochlorate of a new brominated base.

*Dibromomelaniline.*—The solution of the salt just mentioned, deposits, on the addition of ammonia, a white crystalline mass, which separates in white scales from boiling alcohol.

These crystals are *dibromomelaniline.*

$$C_{26}\left\{\begin{matrix}H_{11}\\Br_2\end{matrix}\right\}N_3$$

as the following analysis proves:

0·3980 grm. of the base, when burnt with chromate of lead, gave:
0·6180 „ „ carbonic acid, and
0·1000 „ „ water.

| | Theory. | | Experiment. |
|---|---|---|---|
| 26 equiv. of Carbon . . . . | 156·00 | 42·67 | 42·37 |
| 11 „ „ Hydrogen . . . | 11·00 | 3·00 | 2·80* |
| 3 „ „ Nitrogen . . . . | 42·00 | 11·49 | — |
| 2 „ „ Bromine . . . . | 156·52 | 42·84 | — |
| 1 equiv. of Dibromomelaniline . | 365·52 | 100·00 | |

Dibromomelaniline is nearly insoluble in water; it is dissolved, however, easily by alcohol and ether. These solutions possess a very bitter taste. When heated, this body exhibits a deportment similar to that of melaniline. On raising the temperature above the fusing point of the base, a colourless vapour is evolved, which condenses in the neck of the retort into a colourless liquid, solidifying after some time to a slightly yellow, crystalline mass. These crystals are

* The deficiency of hydrogen was occasioned by the moistening of the cork, which had been kept too cool during the combustion.

pure *bromaniline*. There remains in the retort a resinous mass, of precisely the same appearance as the residue of the distillation of melaniline. This decomposition offers some interest, pointing out, as it does, a method of obtaining *bromaniline*, and, of course, also *chloraniline*, directly from aniline; substances which could hitherto be prepared only by the action of alkalies on chlorinated and brominated isatine.

I have analysed only the hydrochlorate and the platinum compound of dibromomelaniline.

*Hydrochlorate of dibromomelaniline*.—This substance crystallizes in white stellated needles of a silky lustre, which, when deposited from a slowly-cooling solution, sometimes attain the length of a centimetre. They are but slightly soluble in water, and fuse, when boiled in an insufficient quantity, into a yellow oil, which solidifies, on cooling, into a crystalline mass.

The analysis gave the following results:

0·2866 grm. of hydrochlorate of dibromomelaniline gave:
0·1038 „ „ chloride of silver,

which corresponds to 9·2 per cent. of hydrochloric acid.

The formula

$$C_{26}\left\{\begin{matrix}H_{11}\\Br_2\end{matrix}\right\}N_3,\ H\,Cl$$

requires the following numbers:

| | Theory. | | Experiment. |
|---|---|---|---|
| 1 equiv. of Dibromomelaniline . . . | 365·52 | 90·92 | — |
| 1 „ „ Hydrochloric Acid . . . | 36·50 | 9·08 | 9·21 |
| 1 equiv. of Hydrochlorate of Dibromomelaniline . . . . . | 402·02 | 100·00 | |

*Bichloride of platinum and dibromomelaniline*.—A boiling solution of the hydrochlorate gives, with a concentrated solution of bichloride of platinum, an orange-yellow precipitate, which, on cooling, is converted into splendid scales of a golden lustre. This salt is insoluble in water, scarcely soluble in ether, and somewhat more soluble in alcohol.

The analysis yielded the following results:

I. 0·3740 grm. of platinum-salt gave:
0·3768 „ „ carbonic acid, and
0·0781 „ „ water.

II. 0·2220 „ „ platinum-salt yielded:
0·0330 „ „ platinum,

which correspond to the following per centage composition:

| | I. | II. |
|---|---|---|
| Carbon . . . . . | 27·45 | — |
| Hydrogen . . . . | 2·32 | — |
| Platinum . . . . | — | 17·11 |

The formula

$$C_{26}\left\{\begin{matrix}H_{11}\\Br_2\end{matrix}\right\}N_3,\ HCl,\ Pt\ Cl_2$$

requires the following numbers:

| | | | Theory. | | Experiment. |
|---|---|---|---|---|---|
| 26 | equiv. | of Carbon . . . . | 156·00 | 27·28 | 27·45 |
| 12 | „ | „ Hydrogen . . . | 12·00 | 2·09 | 2·32 |
| 3 | „ | „ Nitrogen . . . | 42·00 | 7·38 | — |
| 2 | „ | „ Bromine . . . | 156·52 | 27·37 | — |
| 3 | „ | „ Chlorine . . . | 106·50 | 18·62 | — |
| 1 | „ | „ Platinum . . . | 98·68 | 17·26 | 17·11 |
| 1 eq. of Bichloride of Platinum and Dibromomelaniline | | | 571·70 | 100·00 | |

I have tried to arrest the action of bromine, so as to obtain a compound containing only one equivalent of bromine, by treating a solution of hydrochlorate of melaniline with small quantities of bromine, and adding the ammonia long before any lasting precipitate produced by bromine appeared, in this manner, a precipitate is obtained containing a smaller amount of bromine.

I have converted several of these precipitates into platinum-salts; these salts left, on ignition, slightly varying quantities of platinum, generally shewing a close approximation to the per centage of a monobromomelaniline platinum-salt. I do not, however, feel justified in announcing the existence of such a compound, the products in question not presenting a sufficiently definite character to warrant such affirmation.

These precipitates may just as well have been mixtures of undecomposed melaniline and dibromomelaniline; melaniline being formed by the union of two atoms of aniline, it remains doubtful whether the action of bromine can possibly be confined to one equivalent.

By treating melaniline with an excess of bromine, the substitution-products become less and less basic, until at last a perfectly indifferent resinous body is formed, which I have not analysed. It is, perhaps,

a compound corresponding to tribromaniline, containing six equivalents of bromine. Between this last term of the series and dibromomelaniline, we may assume the existence of several intermediate compounds. The rapidly decreasing property of crystallization in these substances, however, renders a perfect separation almost impossible.

I may still mention the following experiment. A solution of hydrochlorate of melaniline, treated with bromine until it had deposited crystals of the hydrochlorate of dibromomelaniline, was again exposed to the action of bromine. On evaporation, transparent yellow, oily drops were separated, solidifying only after some time to a slightly crystalline mass, the alcoholic solution of which gave, with bichloride of platinum, a resinous precipitate, which likewise became slowly crystalline. In order to purify this, it was dissolved in a large quantity of boiling alcohol, from which it separated, on cooling, in crystalline crusts.

According to the platinum determination, these crystals would be the platinum salt of a tribromomelaniline:

$$C_{26}\left\{\begin{matrix}H_{10}\\Br_3\end{matrix}\right\}N_3$$

0·3824 grm. of platinum-salt left:
0·0574 „ „ platinum,

which gives 15·00 as the per centage of platinum. The calculated per centage is 15·25.

The experimental evidence, however, of the existence of such a compound is likewise insufficient.

*Action of iodine on melaniline.*—I did not succeed in preparing diiodinated melaniline by the action of iodine on melaniline. A solution of the hydrochlorate of this base, when treated with an excess of iodine, deposits a black, sticky mass, scarcely a trace of the base remaining in solution; if the hydrochlorate is gradually mixed with small quantities of an alcoholic solution of iodine, the same precipitate is formed, but the base remaining in solution is unchanged melaniline.

Diiodomelaniline may, however, be easily obtained by treating an ethereal solution of iodaniline with chloride of cyanogen. On passing this gas into the solution, a crystalline precipitate is soon deposited, which is hydrochlorate of iodaniline; by continuing this treatment, these crystals again disappear, and the whole is gradually converted into a resinous mass of hydrochlorate of diiodomelaniline, which slowly becomes crystalline.

The formation of this compound is represented by the following equation:

$$\underbrace{2\left(C_{12}\left\{\begin{matrix}H_6\\I\end{matrix}\right\}N\right)}_{\text{Iodaniline.}} + \underbrace{C_2\,N\,Cl}_{\text{Chloride of Cyanogen.}} = \underbrace{C_{26}\left\{\begin{matrix}H_{11}\\I_2\end{matrix}\right\}N_3,\,H\,Cl}_{\text{Hydrochlorate of Diiodomelaniline.}}$$

Hydrochlorate of diiodomelaniline resembles very much the corresponding salts of the chlorinated and brominated bases. It is very little soluble in water, and separates from the boiling solution in oily drops, which are very slowly converted into beautiful white tufts: I have not examined this salt further.

Diiodomelaniline is separated by ammonia, or better, by potassa, from the preceding hydrochlorate as a white precipitate, which crystallizes from alcohol, though less perfectly than the chlorine- and bromine-bases, which it resembles in every other respect.

The combustion of this compound gave a slight excess of hydrogen, most probably from a small quantity of iodine, which may have been carried over into the chloride of calcium tube.

0·3255 grm. of diiodomelaniline gave:
0·4046 „ of carbonic acid, and
0·0795 „ of water.

The formula:

$$C_{26}\left\{\begin{matrix}H_{11}\\I_2\end{matrix}\right\}N_3$$

requires the following numbers:

| | | Theory. | | Experiment. |
|---|---|---|---|---|
| 26 equiv. of | Carbon . . . . | 156·00 | 33·78 | 33·90 |
| 11 „ „ | Hydrogen . . . | 11·00 | 2·37 | 2·71 |
| 2 „ „ | Iodine . . . . | 252·72 | 54·76 | — |
| 3 „ „ | Nitrogen . . . | 42·00 | 9·09 | — |
| 1 equiv. of | Diiodomelaniline . | 461·72 | 100·00 | |

*Bichloride of platinum and diiodomelaniline.*—To control the above analysis, I prepared the platinum-salt of the iodine base. It resembles the platinum compounds of the chlorine- and bromine-bases, although it is less crystalline.

The analysis of this salt gave the following numbers:

I. 0·2580 grm. of the platinum-salt gave:
0·2195 „ „ carbonic acid, and
0·0490 „ „ water.

II. 0·1310 grm. of platinum-salt left :
0·0192 „ „ platinum.
III. 0·2315 „ „ platinum-salt gave :
0·0340 „ „ platinum.

Per centage composition :

| | I. | II. | III. |
|---|---|---|---|
| Carbon . . | 23·20 | — | — |
| Hydrogen . . | 2·11 | — | — |
| Platinum . | — | 14·66 | 14·68 |

leading to the formula :

$$C_{26}\left\{\begin{matrix}H_{11}\\I_2\end{matrix}\right\}N_3,\ H\,Cl,\ Pt\,Cl_2$$

as may be seen from the following table :

| | | Theory. | | Experiment. |
|---|---|---|---|---|
| 26 equiv. | of Carbon . . . . . | 156·00 | 23·35 | 23·20 |
| 12 „ | „ Hydrogen . . . . | 12·00 | 1·79 | 2·11 |
| 3 „ | „ Nitrogen . . . . | 42·00 | 6·28 | — |
| 2 „ | „ Iodine . . . . . | 252·72 | 37·86 | — |
| 3 „ | „ Chlorine . . . . | 106·50 | 15·95 | — |
| 1 „ | „ Platinum . . . . | 98·68 | 14·77 | 14·67 |
| 1 equiv. of Bichloride of Platinum and Diiodomelaniline . . | | 667·90 | 100·00 | |

*Action of nitric acid on melaniline.*—Common nitric acid dissolves melaniline with considerable evolution of heat; the solution solidifies after a few moments into a hard crystalline mass of the nitrate of melaniline: if a more concentrated, or a large excess of the common acid be employed, or if the solution is heated to ebullition, a most violent reaction ensues, which cannot be kept under control, and the base is converted into a variety of products.

The action of fuming nitric acid on melaniline is so powerful, that, if equal parts of acid and base are mixed, an explosion takes place, the melaniline being entirely decomposed with the evolution of a column of black smoke. By gradual treatment with fuming acid, melaniline, according to the time the action lasts, is converted, either into a magnificent new base, crystallizing in short prisms of an orange-yellow colour and violet irridescence; or into brownish-yellow crystals of a new acid, which forms scarlet salts with alkalies. In the commencement, I thought that the base produced in this reaction was dinitromelaniline; a more minute investigation shewed, however, that it bears a different relation to melaniline from that of a simple substitution-product.

For this reason, I refrain from following for the present the action of nitric acid on melaniline any further. The nitro-base, corresponding to dichloromelaniline, is formed, as was to be expected, by the action of chloride of cyanogen on nitraniline.

*Dinitromelaniline.*—The manner in which chloride of cyanogen is permitted to act on nitraniline, is by no means a matter of indifference; the simplest method appeared to be, to pass the gas through the fused base. Dinitromelaniline is, indeed, formed in this process; a large quantity of the nitraniline, however, seems to undergo, in this case, another decomposition. An aqueous solution of nitraniline undergoes a peculiar decomposition with chloride of cyanogen, which I intend to investigate more fully at a future period; an alcoholic solution is very slowly attacked. I found it most advantageous to employ an ethereal solution; on passing a current of chloride of cyanogen through an ethereal solution of nitraniline, until nearly the whole of the ether has been evaporated in the air accompanying the chloride, a residue is obtained, which contains two new bodies mixed with more or less of unchanged nitraniline. The residue, when heated with an insufficient quantity of water, fuses into a brown oil, which dissolves, however, almost completely in a considerable amount of boiling water.

This solution deposits yellowish needles on cooling, which we will only mention for the present. The colourless mother-liquor of this body contains the hydrochlorate of dinitromelaniline, which separates on the addition of ammonia, in the form of a bright sulphur-yellow precipitate, rapidly becoming crystalline.

These crystals may possibly still contain some nitraniline which has escaped decomposition; it can be easily separated by treatment with boiling water, in which the new product is perfectly insoluble.

The analysis of the base itself, as well as of the hydrochlorate and of the platinum-salt, leaves not the slightest doubt respecting the nature of this compound.

0·2393 grm. of the substance gave:
0·4538 „ „ carbonic acid, and
0·0854 „ „ water.

The composition per cent. is therefore:

| | |
|---|---|
| Carbon . . . . | 51·71 |
| Hydrogen . . . | 3·96 |

leading to the formula:

$$C_{26}\left\{\begin{matrix}H_{11}\\2\,NO_4\end{matrix}\right\}N_3,$$

which requires the following numbers:

| | Theory. | | Experiment. |
|---|---|---|---|
| 26 equiv. of Carbon . . . . . | 156 | 51·82 | 51·71 |
| 11 „ „ Hydrogen . . . . . | 11 | 3·65 | 3·96 |
| 5 „ „ Nitrogen . . . . . | 70 | 23·25 | — |
| 8 „ „ Oxygen . . . . . | 64 | 21·28 | — |
| 1 equiv. of Dinitromelaniline . . . | 301 | 100·00 | |

The formation of this compound is perfectly analogous to that of melaniline and diiodomelaniline.

$$2\underbrace{\left(C_{12}\left\{\begin{matrix}H_6\\NO_4\end{matrix}\right\}N\right)}_{\text{Nitraniline.}} + \underbrace{C_2NCl}_{\substack{\text{Chloride}\\\text{of Cyanogen.}}} = \underbrace{C_{26}\left\{\begin{matrix}H_{11}\\2\,NO_4\end{matrix}\right\}N_3, HCl}_{\substack{\text{Hydrochlorate of}\\\text{Dinitromelaniline.}}}$$

The new nitro-base, when precipitated from the hydrochlorate by ammonia or potassa, appears as a scaly crystalline mass. It is at once distinguished from nitraniline by its brighter colour. It is difficultly soluble in alcohol, and still less soluble in ether. From the alcoholic solutions it is precipitated by water in the form of a splendid crystalline mass, possessing the lustre of metallic gold. Dinitromelaniline is unquestionably the most beautiful product of the whole series. The crystals which have been precipitated from an alcoholic solution by water appear under the microscope as short, flat needles; crystals of the same shape, but much larger, may be obtained by allowing an ethereal solution of the base to evaporate spontaneously in narrow vessels.

The solutions of the base in alcohol and ether possess a deep yellow colour.

Dinitromelaniline is not volatile without decomposition. When heated, it undergoes a change similar to that of melaniline; a yellow vapour is evolved, condensing on the cooler parts of the retort into brown, oily drops, which gradually become crystalline, whilst a brown, resinous substance remains in the retort. The crystalline product of decomposition is soluble in acids, from which it is reprecipitated by ammonia as a yellow substance, gradually crystallizing in long needles. It is *nitraniline*.

Dinitromelaniline forms, with most acids, well crystallizable salts, which in the solid state, as well as in solution, are perfectly colourless. I have analysed only two of them.

*Hydrochlorate of dinitromelaniline.*—This salt crystallizes in flattened needles or plates of considerable lustre, and which are

rather difficultly soluble, whilst the corresponding salt of nitraniline dissolves with the greatest facility.

0·2893 grm. of substance gave:
0·1230 „ „ chloride of silver,

equivalent to 10·82 per cent of hydrochloric acid, which corresponds closely with the formula:

$$C_{26}\left\{\begin{matrix}H_{11}\\2\,NO_4\end{matrix}\right\}N,HCl,$$

as is shown by the following table:

| | Theory. | | Experiment. |
|---|---|---|---|
| 26 equiv. of Carbon . . . . | 156·00 | 46·22 | — |
| 11 „ „ Hydrogen . . . . | 11·00 | 3·26 | — |
| 5 „ „ Nitrogen . . . . | 70·00 | 20·74 | — |
| 8 „ „ Oxygen . . . . | 64·00 | 18·97 | — |
| 1 „ „ Hydrochloric acid . | 36·50 | 10·81 | 10·82 |
| 1 eq. of Hydrochlorate of Dinitromelaniline . . . . | 337·50 | 100·00 | |

*Bichloride of platinum and dinitromelaniline.*—The solution of the preceding salt gives a yellow crystalline precipitate with bichloride of platinum, which is insoluble in water and alcohol, and only slightly soluble in ether. The platinum-salt of nitraniline is very soluble in water. The platinum-salt of dinitromelaniline, when heated, is decomposed with a slight deflagration: in determining the platinum, it was, therefore, necessary to ignite only a small quantity at a time in a covered platinum crucible. A determination of this kind gave the following results:

0·097 grm. of the salt, gave:
0·019 „ „ platinum.

In 100 parts, therefore, 19·58, agreeing with the formula:

$$C_{26}\left\{\begin{matrix}H_{11}\\2\,NO_4\end{matrix}\right\}N,\ HCl,\ Pt\ Cl_2,$$

as may be seen by the following table:

| | Theory. | | Found. |
|---|---|---|---|
| 26 equiv. of Carbon . . . . . | 156·00 | 30·76 | — |
| 13 „ „ Hydrogen . . . . | 12·00 | 2·38 | — |
| 5 „ „ Nitrogen . . . . . | 70·00 | 13·60 | — |
| 8 „ „ Oxygen . . . . . | 64·00 | 12·62 | — |
| 3 „ „ Chlorine . . . . , . | 106·50 | 21·19 | — |
| 1 „ „ Platinum . . . . . | 98·68 | 19·45 | 19·58 |
| 1 eq. of Bichloride of Platinum and Dinitromelaniline . . . | 507·18 | 100·00 | |

Of the other salts of dinitromelaniline, I have prepared only the nitrate, sulphate, and oxalate. The nitrate is difficultly soluble, like the corresponding salt of nitraniline, and crystallizes in indistinct needles. The sulphate and oxalate dissolve very readily in water, the former being deposited in crystals, the latter in granular tufts.

*Action of cyanogen on melaniline.*—The peculiar comportment of cyanogen with aniline and the analogous bases, with which I had become acquainted in former experiments, induced me to act with the same gas on melaniline; my principal object being to gain by this means another instance of this peculiar mode of action.

A cold saturated alcoholic solution of melaniline absorbs a very large quantity of cyanogen gas; the saturated liquid, when kept in a corked bottle, soon deposits yellowish crystalline crosses, of a satin lustre; and, after the lapse of a few hours, the whole solution solidifies to a soft crystalline mass: the odour of the cyanogen has now disappeared, whilst that of prussic acid is perceptible.

Dicyanomelaniline, the new substance, is insoluble in water; it dissolves, however, rather easily in boiling alcohol. In order to purify it, the brown mother-liquor is drained from the crystals, which are washed with cold alcohol. Two or three crystallizations from the same solvent (boiling) render the substance perfectly pure.

For the following analyses, specimens of different preparations were employed:

I. 0·4051 grm. of substance gave:
1·0200 „ „ carbonic acid, and
0·1980 „ „ water.
II. 0·2544 „ „ substance gave:
0·6411 „ „ carbonic acid, and
0·1180 „ „ water.
III. 0·3309 „ „ substance gave:
0·8252 „ „ carbonic acid, and
0·1525 „ „ water.
IV. 0·2760 „ „ substance gave:
0·6880 „ „ carbonic acid, and
0·1200 „ „ water.

In 100 parts:

| | I. | II. | III. | IV. |
|---|---|---|---|---|
| Carbon . . . . | 68·67 | 68·72 | 68·01 | 67·98 |
| Hydrogen . . . | 5·29 | 5·15 | 5·12 | 4·83 |

which lead to the formula:

$$C_{30}\,H_{13}\,N_5 = Cy_2,\,C_{26}\,H_{13}\,N_3,$$

as may be seen from the following table:

| | Theory. | | Experiment. |
|---|---|---|---|
| 30 equiv. of Carbon . . . . . | 180 | 68·44 | 68·34 |
| 13 „ „ Hydrogen . . . . . | 13 | 4·94 | 5·13 |
| 5 „ „ Nitrogen . . . . . | 70 | 26·62 | — |
| 1 equiv. of Dicyanomelaniline . . . | 263 | 100·00 | |

Dicyanomelaniline (which name I propose for the new substance) is simply melaniline which has united with two equivalents of cyanogen; its formation is perfectly analogous to that of cyaniline. The assimilation of two equivalents of cyanogen is remarkable, although perfectly in accordance with the structure of melaniline.

It appears that both the aniline atoms (the intimate combination of which constitutes melaniline,) still exhibit the same comportment with cyanogen as when in the isolated state, and if it be permitted to express an opinion respecting the probable arrangement of the elements by a formula, the constitution of dicyanomelaniline may be represented by the following expression:

$$Cy\ C_{12}\ H_7\ N,\ Cy\ C_{12}\ H_6\ N\ Cy.$$

Dicyanomelaniline, when pure, forms slightly yellowish needles; the colour seems to be peculiar to the compound, it cannot be separated by repeated treatment with animal charcoal. Like the other melaniline products, it is not volatile without decomposition; when heated, aniline and cyanide of ammonium are disengaged, while a resinous body remains in the retort, which chars at a higher temperature.

In dicyanomelaniline, the basic properties of melaniline are still perceptible: they appear, however, less prominent than in the descendants by substitution. The cyanogen base dissolves with great facility in dilute acids in the cold; on adding ammonia to the acid solution, a few moments after it has been made, a white precipitate is thrown down, consisting of unaltered dicyanomelaniline. I have, however, vainly tried to prepare salts of this base.

When describing the compounds of cyaniline, I mentioned that this base cannot remain in acid solutions, without soon undergoing complete decomposition. The same comportment was exhibited in a far more decided manner with dicyanomelaniline. The clear solution of this base, in hydrochloric acid, deposits, after a few

minutes, a yellow, slightly crystalline powder, which is by no means a hydrochlorate: the same metamorphosis ensues instantaneously on ebullition. If a boiling alcoholic solution of dicyanomelaniline is mixed with an excess of hydrochloric acid, the liquid assumes a perfectly yellow colour, and, on cooling, beautiful white needles of another new body are deposited. In both cases, the mother-liquor contains large quantities of ammonia.

For a more complete development of these peculiar decompositions, a few data are still wanting at this moment, for which reason I refrain, at present, from any further details. I intend to return to this subject as soon as I shall have placed before the Society a description of the phenomena attending the decomposition of cyaniline, which, although simpler, present a certain degree of analogy with the above-mentioned changes. But I may mention even now, that the products arising from the decomposition of dicyanomelaniline belong to the most remarkable substances which have been brought to light by this investigation.

The comportment of melaniline, with other reagents, I have as yet only studied cursorily. To complete this investigation, a great number of experiments have to be performed; the behaviour, especially, which melaniline and its descendants exhibit under the influence of heat, requires a very close investigation. I have frequently alluded to this decomposition, with the study of which I am now engaged.

It is not unlikely that the residue in the retort is the mellon of the aniline series. If we recollect that melamine, when exposed to dry distillation, is split up into ammonia and mellon:

$$\underbrace{C_6\,H_6\,N_6}_{\text{Melamine.}} = \underbrace{C_6\,N_4}_{\text{Mellon.}} + 2\,\underbrace{NH_3}_{\text{Ammonia.}},$$

the idea naturally suggests itself, that an analogous decomposition may take place with melaniline:

$$3\,\underbrace{C_{36}\,H_{13}\,N_3}_{\text{Melaniline.}} = \underbrace{\begin{matrix} C_{78}\,H_{39}\,N_9 - \\ C_{60}\,H_{35}\,N_5 \end{matrix}}_{C_{18}\,H_4\,N_4} = \underbrace{5\,C_{12}\,H_7\,N}_{\text{Aniline.}}$$

$$= \underbrace{C_{12}\,H_4, C_6\,N_4}_{\text{Anilo-Mellon.}}$$

These, however, are speculations unsupported as yet by experiment.

*Action of bromide of cyanogen on aniline.*—I have ascertained, by experiment, that in this reaction exactly the same products are formed as with the chloride. The action proceeds only more slowly, owing to the inferior affinity of bromine for hydrogen. On treating with water, the crude product of the action of Serullas' bromide, (prepared by the action of bromine on moistened cyanide of mercury), a solution of hydrobromate of melaniline is obtained:

$$\underbrace{2\,C_{12}\,H_7\,N}_{\text{Aniline.}} + \underbrace{C_2\,N\,Br}_{\substack{\text{Bromide of}\\ \text{Cyanogen.}}} = \underbrace{C_{26}\,H_{13}\,N_3,\,HBr.}_{\substack{\text{Hydrobromate of}\\ \text{Melaniline.}}}$$

After precipitating the base from this solution, by potassa, the mother-liquor deposits, on evaporation, the same indifferent body which I have mentioned when speaking of the action of the chloride. Although the properties of the base, obtained by means of bromide of cyanogen, did not admit of any doubt regarding its identity with melaniline, I have, nevertheless, made a determination of platinum:

| | |
|---|---|
| Platinum-salt employed . . . . | 0·3316 |
| Platinum obtained . . . . . | 0·0786 |

which corresponds to the following per centage composition:

| | Theory. | Experiment. |
|---|---|---|
| Per centage of platinum in the melaniline double salt . . . | 23·65 | 23·70 |

*Action of iodide of cyanogen on aniline.*—I have repeatedly treated aniline with iodide of cyanogen, which may be easily procured in any quantity by Liebig's process, viz., by dissolving iodine in a solution of crude cyanide of potassium. Iodide of cyanogen, however, is not capable of converting aniline into melaniline. In all my experiments, iodaniline only was formed, together with hydrocyanic acid, and a brown iodinated product of decomposition:

$$\underbrace{C_{12}\,H_7\,N}_{\text{Aniline.}} + \underbrace{Cy\,I}_{\substack{\text{Iodide of}\\ \text{Cyanogen.}}} = \underbrace{C_{12}\left\{\begin{matrix}H_6\\ I\end{matrix}\right\}N}_{\text{Iodaniline.}} + \underbrace{HCy.}_{\substack{\text{Hydrocyanic}\\ \text{Acid.}}}$$

For the determination of platinum, No. II., mentioned in my paper on iodaniline, the base had been prepared by the action of iodide of cyanogen on aniline.

The following is a synoptical table of the members of the melaniline group which have as yet been studied:

| | | | | |
|---|---|---|---|---|
| Melaniline . . . . | $C_{12}\ H_7\ N, C_{12}\ H_6\ N, Cy,$ | | | |
| Sulph. of melan. . . | $C_{12}\ H_7\ N, C_{12}\ H_6\ N, Cy,$ | $H\ SO_4$ | | |
| Nitr. of melan. . . | $C_{12}\ H_7\ N, C_{12}\ H_6\ N, Cy,$ | $H\ NO_6$ | | |
| Binox. of melan. . . | $C_{12}\ H_7\ N, C_{12}\ H_6\ N, Cy,$ | $2(H\ C_2\ O_4)$ | | |
| Hydrochl. of melan. . | $C_{12}\ H_7\ N, C_{12}\ H_6\ N, Cy,$ | $H\ Cl$ | | |
| Hydrobrom. of melan. | $C_{12}\ H_7\ N, C_{12}\ H_6\ N, Cy,$ | $H\ Br$ | | |
| Hydriodate of melan. . | $C_{12}\ H_7\ N, C_{12}\ H_6\ N, Cy,$ | $H\ I$ | | |
| Platinum-salt . . . | $C_{12}\ H_7\ N, C_{12}\ H_6\ N, Cy,$ | $H\ Cl,$ | $Pt\ Cl_2$ | |
| Gold-salt . . . . | $C_{12}\ H_7\ N, C_{12}\ H_6\ N, Cy,$ | $H\ Cl,$ | $Au\ Cl_3$ | |
| Silver-salt . . . | $2(C_{12}\ H_7\ N, C_{12}\ H_6\ N, Cy,)$ | $Ag\ NO_6$ | | |
| Dichloromelaniline . | $C_{12}\{H_6 Cl\}N, C_{12}\{H_5 Cl\}N, Cy,$ | | | |
| Platinum-salt . . . | $C_{12}\{H_6 Cl\}N, C_{12}\{H_5 Cl\}N, Cy,$ | $H\ Cl,$ | $Pt\ Cl_2$ | |
| Dibromomelaniline . | $C_{12}\{H_6 Br\}N, C_{12}\{H_5 Br\}N, Cy,$ | | | |
| Hydrochl. of dibrom. . | $C_{12}\{H_6 Br\}N, C_{12}\{H_5 Br\}N, Cy,$ | $H\ Cl,$ | | |
| Platinum-salt . . . | $C_{12}\{H_6 Br\}N, C_{12}\{H_5 Br\}N, Cy,$ | $H\ Cl,$ | $Pt\ Cl_2$ | |
| Diiodomelaniline . . | $C_{12}\{H_6 I\}N, C_{12}\{H_5 I\}N, Cy,$ | | | |
| Platinum-salt . . . | $C_{12}\{H_6 I\}N, C_{12}\{H_5 I\}N, Cy,$ | $H\ Cl,$ | $Pt\ Cl_2$ | |
| Dinitromelaniline . . | $C_{12}\{H_6 NO_4\}N, C_{12}\{H_5 NO_4\}N, Cy,$ | | | |
| Hydrochl. of dinitrom. | $C_{12}\{H_6 NO_4\}N, C_{12}\{H_5 NO_4\}N, Cy,$ | $H\ Cl,$ | | |
| Platinum-salt . . . | $C_{12}\{H_6 NO_4\}N, C_{12}\{H_5 NO_4\}N, Cy,$ | $H\ Cl,$ | $Pt\ Cl_2$ | |
| Dicyanomelaniline . . | $C_{12}\ H_7\ N, C_{12}\ H_6\ N, Cy,$ | $\{Cy Cy$ | | |

Melaniline is a conjugated base of a similar, although more complicated, constitution than cyaniline which I have recently described. But while in the latter case, the aniline atom has only assimilated an equivalent of cyanogen, we find it, in the former, associated with a complex compound of cyanogen, viz., with cyanilide. And this capability, which we observe in aniline, of combining with other substances without losing its basic properties, has by no means reached its limits in melaniline; in dicyanomelaniline, we see two new equivalents of cyanogen enter into the compound, and some preliminary experiments appear to indicate that this accumulation round the original atom may be carried still farther.

Facts, like these, deserve particular attention, containing, as they

do, new confirmations of a general view of the organic bases which is daily gaining ground.

At a very early period, as far back as 1837, Berzelius, on the ground of Liebig's researches, expressed the opinion, that the natural alkaloids, which at that period engrossed the undivided attention of chemists, were peculiar ammonia-compounds—conjugated compounds, in which the chemical character of ammonia, modified indeed by its conjunct, was still perceptible.

This view, which was principally founded on the remarkable analogy of the ammonia-salts and the salts of the alkaloids, met by no means with general approbation when first started; but it has been retained and carried out by Berzelius, with the perseverance and ratiocination which are peculiar to that great chemist. And it cannot be denied that since that period, science has acquired a great number of facts which powerfully support his opinion.

Organic chemistry has been enriched by a long and daily increasing series of artificial bases formed in a variety of processes, many of which products we see generated by the direct action of ammonia on other compounds; protochloride of platinum, when acted on by ammonia, gives rise to the various bases of Gros's and Reiset's salts; the ammonia-compound of cyanic acid, urea, is endowed with all the properties of the natural alkaloids. The ethereal oil of mustard, on combining with ammonia, is converted into thiosinnamine, (rhodalline, Berzelius) a weak organic base; and it is not unlikely that thialdine, the remarkable basic compound which Liebig and Wöhler * obtained but lately by the action of hydrosulphuric acid on aldehydite of ammonia, must be considered as the ammonia compound of garlic oil. In a similar manner the bases, furfurine and picramine, (amarine, benzoline), are formed by the action of ammonia on furfurol, or oil of bitter almonds. And here we observe the remarkable phenomenon, that the direct products of this action, viz., furfuramide and hydrobenzamide are merely neutral substances, which, as the beautiful investigation of Professor Fownes has taught us, are converted only by the action of caustic alkalies into basic bodies, possessing exactly the same composition, but perfectly different physical properties. Hence, it appears, that in furfuramide and hydrobenzamide, nitrogen is no longer contained in the form of ammonia. From the transition of these indifferent substances into bases, under the influence of reagents, giving rise in so many cases to the formation of ammonia, does it not become exceedingly probable, that, in this case, part of the nitrogen has been re-converted into ammonia, which, uniting

* Mem. of the Chem. Soc., vol. III.

with the remaining elements, has impressed its character on the whole compound?

It is scarcely to be doubted, that the natural alkaloids, which we separate from plants, are formed in a similar manner. All the juices of plants contain more or less ammonia, by the action of which on the acids, on the indifferent principles, or on the ethereal oils, likewise contained in these juices, the generation of so numerous a class of bodies like the organic alkaloids, may be explained without difficulty.

Another series of researches has pointed out the close analogy between ammonia and the organic bases in a still more striking manner. Several years ago, I observed, that by the action of cyanic acid on aniline, a compound was produced, which, from its properties, cannot be considered as cyanate of aniline, although it has exactly the composition of that salt.

The caustic alkalies, in the cold at least, evolve no aniline from this compound; mineral acids disengage neither cyanic acid nor its products of decomposition, a deportment which is sufficient to distinguish this compound from cyanate of aniline.

This body evidently bears to aniline the same relation which urea bears to ammonia; it is the urea of the aniline series:

| | |
|---|---|
| Urea . . . . | $N H_3, C_2 H NO_2$ |
| Aniline-urea . . | $N H_3, C_2 H NO_2 (C_{12} H_4)$ |

instances of a similar kind were soon found in abundance.

The deportment of ammonia with the metals of the alkalies, shews that one equivalent of hydrogen in this body is in a peculiar state of mobility, which admits of its easy elimination and replacement by other substances, a class of compounds being thus produced, which we designate by the name of amides.

Exactly the same phenomenon is observed with aniline. On introducing potassium into anhydrous aniline, I observed* a copious evolution of hydrogen, the base being converted into a viscid mass, capable of being decomposed by water, which was evidently the aniline compound corresponding to amide of potassium.

| | |
|---|---|
| Amide of potassium . . | $K, NH_2,$ |
| Anilide of potassium . . | $K, NH_2, (C_{12} H_4)$ |

The dry distillation of ammoniacal salts has elicited a series of compounds, which can likewise be reproduced with the organic bases. Under the influence of temperatures of different intensities, neutral salts of oxide of ammonium lose either two or four equivalents

* Liebig's Annalen, LVII.

of water; we obtain, in the first case, amides; in the second case, the class of substances which are at present designated by the name of nitriles.

Acid ammonia-salts, when distilled, exhibit exactly the same phenomenon; they are converted by the elimination of two equivalents of water into amidogen-acids; by the abstraction of four equivalents, into imidogen-compounds.

For all these classes, numerous and well-characterized representatives are known. Dumas' *oxamide*, and *benzamide*, discovered by Liebig and Wöhler, are still prototypes of the first class. The second is represented by *cyanogen* (Döbereiner); *prussic acid* (Pelouze); *benzonitrile* (Fehling); *valeronitrile* (Schlieper); *cumonitrile* (Field); and several compounds discovered lately by Dumas, Malaguti, and Leblanc. The first instance of the third group was *oxamic acid*, discovered by Balard, to which were soon added numerous members by Piria (*malamic acid*), and by Laurent (*tartaramic acid, camphoramic acid*); and it is to the latter chemist that we are chiefly indebted for a lucid development of the theory of these acids. The imidogen-compounds are as yet the least known: the first, *benzimide*, was discovered many years ago by Laurent, who afterwards found another instance in camphorimide; cyanic acid (derived from bicarbonate of oxide of ammonium) may also be considered as belonging to this class. With no one acid have all the four classes of compounds as yet been obtained; with oxalic acid and benzoic acid, we find them best represented: with the former, only *oximide* is wanting, whilst the latter still requires *benzamic acid** for its completion.

Now it appears that these compounds, into which ammoniacal salts are converted by the loss of water, may likewise be obtained with organic bases, or, in other words, (adopting the theory of Berzelius), ammonia, by conjugation, has not lost its original properties, its hydrogen being still capable of elimination by the oxygen of acids.

By distilling oxalate of aniline, M. Gerhardt obtained a compound which he called oxanilide, and which, in every respect, represents the oxamide of the ammonia series.

| | |
|---|---|
| Oxamide . . . . | $NH_2, C_2 O_2$ |
| Oxanilide. . . . | $NH_2, C_2 O_2, (C_{12} H_4)$ |

With chloride of benzoyl, aniline is converted into an analogue of benzamide.

* Under this name, M. Zinin has described an acid obtained by acting with sulphuretted hydrogen on nitrobenzoic acid; but, as Berzelius justly observes, this acid should receive another name.

Benzamide . . . $NH_2$, $C_{14}$ $H_5$ $O_2$
Benzanilide . . . $NH_2$, $C_{14}$ $H_5$ $O_2$ ($C_{12}$ $H_4$).

I have performed the same experiment at various periods in the course of these investigations, and can most fully confirm the above statements.

This class of compounds is rapidly increasing, and the anilides seem to be formed even with more facility, and to be more stable, than the corresponding amides.

It is well known that carbamide, produced by the action of ammonia on phosgene gas, cannot be easily separated from the accompanying chloride of ammonium, and that it is very easily decomposed; I found, on the contrary, no difficulty in preparing, by the same process, the corresponding carbanilide, which is moreover a very stable compound.

Carbamide . . . $NH_2$, CO
Carbanilide . . . $NH_2$, CO ($C_{12}$ $H_4$).

By acting with bisulphide of carbon on aniline, I obtained sulphocarbanilide; the corresponding member in the ammonia series is as yet unknown. The same holds good with several other similar compounds.

All the bases analogous to aniline will, most likely, show the same comportment. Even now, several napthalidides have been studied by Mr. Delbos, and Mr. Nicholson has pointed out the existence of various cumidides.

The compounds corresponding to cyanogen are as yet scarcely known, probably, because a sufficient number of experiments have not been made with a view to their production.

If oxalate of aniline is rapidly distilled, the peculiar odour, which I have repeatedly mentioned, is developed in a most powerful manner. A mixture of oxanilide and anhydrous phosphoric acid yields, on distillation, a small quantity of this exceedingly pungent compound in the form of oily drops, which, after some time, solidify to a crystalline mass. Unfortunately the largest quantity of oxanilide is charred in this experiment, and the small quantity of the product has, as yet, prevented a close examination of this body. Experiments with chloride of zinc have not given more satisfactory results. This body appears, however, in large quantity among the products of decomposition of dicyanomelaniline, so that I hope soon to be able to give a detailed account of it to the Society.

We know already several conjugated amidogen-acids. Allophanic acid, lately studied by Liebig and Wöhler, is, in the sense of Berzelius' theory, carbamic acid with urea as a conjunct; *i. e.* it is derived

from carbamic acid by the entrance of the same conjunct which converts ammonia into urea, viz., cyanic acid:

Carbamic acid . . . $NH_2\,CO,\ CO_2,\ HO$
Allophanic acid . . $NH_2\,CO,\ CO_2,\ HO,\ (C_2\,N\,H\,O_2)$.

In the same manner, oxaluric acid may be considered as a conjugated oxamic acid of the same kind.

Oxamic acid . . . . $NH_2\,C_2\,O_2,\ C_2\,O_3,\ HO$
Oxaluric acid . . . $NH_2\,C_2\,O_2,\ C_2\,O_3,\ HO\ (C_2\,N\,HO_3)$.

It deserves to be investigated, whether this acid, which as yet has emerged only from the products of decomposition of uric acid, may not be obtained likewise, either by the dry distillation of an acid oxalate of urea, or by acting with cyanic acid on oxamic acid. Some experiments, which are just now in progress in my laboratory, will, I hope, decide this question.

Conjugated imidogen-compounds have not as yet been described; but I may mention even now, that various substances belonging to this group appear among the products of the decomposition of dicyanomelaniline.

All these considerations render it exceedingly probable that the organic bases are indeed conjugated ammonia-compounds. It is true we are not able, at present, to isolate the ammonia without entirely destroying the compounds; and it is a question whether we shall ever find a method of separating and re-uniting the proximate constituents which the theory of Berzelius supposes in these alkaloids, in the same manner as we effect the separation and re-union of acid and base in a salt. Vainly have I hoped, in the course of my investigations on this subject, to see aniline split up into ammonia and the conjunct

$$C_{12}\,H_4.$$

Possibly this separation may succeed in the hands of a more happy experimenter; possibly it may ever remain unaccomplished: nevertheless, the adoption of Berzelius' theory will prove a great benefit, even if it were only to aid the memory and to facilitate the study.

All our formulæ, our whole nomenclature, would be simplified by such an adoption. No longer should we have anilides, naphthalidides and cumidides; these substances becoming anilo-amides, napthalido-amides, and cumido-amides; and by introducing conventional symbols for the conjuncts, every compound might be expressed rapidly and concisely.

By considering the alkaloids as conjugated compounds of ammonia, cyaniline and melaniline become conjugated ammonia-compounds of the second order, or, in other words, the original ammonia-atom has

become associated with the conjunct, $C_{12} H_4$ = An, and with other substances, and the rational formulæ of these compounds now assume the following shape:

| | |
|---|---|
| Ammonia . . . . | $N H_3$ |
| Aniline . . . . | $N H_3$, (An) |
| Cyaniline . . . . | $N H_3$, (An, Cy) |
| Melaniline . . . | $N H_3$, ($An_2$, Ad Cy) |
| Dicyanomelaniline . | $N H_3$, (2 An Cy, Ad Cy). |

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## XIV.—*On the Compounds of Phosphoric Acid with Aniline.*

By Edward Chambers Nicholson, Esq.

(Read before the Chemical Society of London.)

Of the inorganic acids there is none so remarkable for the number and variety of the compounds it forms with bases as phosphoric acid. The peculiar and complex reactions of the salts of this acid were first satisfactorily explained by Professor Graham, in his well-known paper published in 1833.* The modifications of phosphoric acid by its amount of water of hydration, giving rise to pyrophosphoric and metaphosphoric acid, beautifully explained all that was enigmatical in the observed reactions.

Professor Graham's excellent experiments have added a great deal to our knowledge of phosphoric acid; the study, however, of this acid and its salts is by no means exhausted. I consequently hope that any contribution to the subject will be accepted.

The following experiments, which were instituted in the laboratory of the Royal College of Chemistry, relate to the combination of phosphoric acid with a large and interesting group of bodies, viz., the organic alkaloids. It is curious that this class of salts has not been hitherto examined; indeed the composition of scarcely any phosphate of an organic base has been satisfactorily ascertained.

It was a very interesting question, whether these bases, which with monobasic acids comport themselves exactly like mineral oxides, were capable of combining with polybasic acids in the same remarkable proportions. In the absence of experiments, the only

* Phil. Trans. of Royal Society of London, Part II, 1833. Researches on the Arseniates, Phosphates and Modifications of Phosphoric Acid, by Thomas Graham, Esq., M.A., F.R.S.E., Professor of Chemistry in the Andersonian University of Glasgow.

points which were known from whence we might, by way of analogy, have inferred any similarity in these compounds with the inorganic phosphates, are the salts of ammonia with phosphoric acid; ammonia being as it were the type of all the organic bases. A phosphate of ammonia indeed is known, containing two equivalents of the volatile alkali; but it still remained to be decided whether any true organic alkaloid unites in the proportions of two or more equivalents with one equivalent of phosphoric acid.

The only analysis of a phosphate with an organic alkali has been published by Regnault.* This chemist determined the carbon and hydrogen in phosphate of strychnine. Regnault considered the salt, which he analysed, as a compound of 1 equiv. of phosphoric acid, 1 equiv. of strychnine and water,

$$H, C_{43} H_{23} N_2 O_4, PO_6.$$

However, Regnault's formula of strychnine has subsequently been corrected by Professor Liebig†, who showed that this base contains one equivalent of carbon more, *i. e.*

$$C_{44} H_{23} N_2 O_4;$$

it is, therefore, evident that the composition of Regnault's phosphate is to be expressed by the formula:

$$H, C_{44} H_{23} N_2 O_4, 2H, PO_8,$$

as Professor Liebig‡ already remarks, and, as may be seen from the following comparison of the per centages corresponding to this formula with his analytical results, which I have calculated with the new atomic weights of carbon:

| | | Theory. | | Experiment. |
|---|---|---|---|---|
| 44 equiv. of Carbon . . . | | 264 | 59·19 | 59·85 |
| 26 „ „ Hydrogen . . | | 26 | 5·83 | 5·85 |
| 2 „ „ Nitrogen . . | | 28 | 6·27 | — |
| 12 „ „ Oxygen . . | | 96 | 21·53 | — |
| 1 „ „ Phosphorus . | | 32 | 7·18 | — |
| 1 equiv. of Phosphate of Strychnine . . . | | 446 | 100·00 | |

It is evident from these numbers that the phosphate of strychnine, analysed by Regnault, is a common phosphate, corresponding to the phosphate of soda with 1 equiv. of fixed base.

It being a matter of indifference whether the base, which I took for

* Liebig's Annalen, vol. xxvi, p. 37. † Ibid. vol. xxvi, p. 58.
‡ Handwörterbuch der Chemie, Artikel "Organic Bases," vol. i, p. 70.

experiment was a natural alkaloid or one prepared artificially in the laboratory, I selected aniline, deeming it especially suited to my purpose, as this base generally forms with acids readily crystallizable compounds.

### I. COMPOUNDS OF TRIBASIC PHOSPHORIC ACID WITH ANILINE.

#### 1. PHOSPHATE WITH 2 EQUIVS. OF ANILINE AND 1 EQUIV. OF HYDROGEN.

On adding aniline in excess to a strong solution of tribasic phosphoric acid, the whole instantly solidified to a white crystalline mass, which was drained, pressed, dissolved in a large quantity of boiling dilute alcohol, and filtered through a warm funnel; on cooling, the whole became a mass of crystals; after pressing these between folds of bibulous paper, I finally dried them on a warm porous tile.

When dry, this salt appears as beautiful flesh-coloured nacreous plates, which might be readily taken for thionurate of ammonia, it is quite inodorous and slightly acid to test paper. The crystals are very soluble in ether and water, sparingly soluble in cold alcohol, but very soluble in hot, so that upon cooling, the whole liquid becomes solid. This salt cannot be dried at 100° C. (212° F.), because at this temperature it gives off aniline, assuming a red colour. It melts at a gentle heat, and upon raising the temperature gives off its aniline, and leaves metaphosphoric acid.

When burnt with protoxide of copper:

I. 0·419 grm. of substance gave:
0·774 „ „ carbonic acid, and
0·227 „ „ water.
II. 0·646 „ „ substance gave:
1·183 „ „ carbonic acid, and
0·356 „ „ water.
III. 1·000 „ neutralized with ammonia and precipitated with nitrate of silver, gave:
1·461 „ of tribasic phosphate of silver.

These numbers correspond with the following per centage composition:

| | I. | II. | III. |
|---|---|---|---|
| Carbon . . . | 50·38 | 49·94 | — |
| Hydrogen . . | 6·01 | 6·19 | — |
| Phosphorus . | — | — | 24·86 |

leading to the formula:

$$2\,(H, C_{12} H_7 N), H, PO_8,$$

as is seen by the following comparison:

| | | Theory. | | Experiment. |
|---|---|---|---|---|
| 24 equiv. | of Carbon . . . | 144 | 50·53 | 50·16 |
| 17 „ | „ Hydrogen . . | 17 | 5·97 | 6·10 |
| 2 „ | „ Nitrogen . . . | 28 | 9·83 | — |
| 8 „ | „ Oxygen . . . | 64 | 22·45 | — |
| 1 „ | „ Phosphorus . . | 32 | 11·22 | 11·13 |
| 1 eq. of Phosphate of Aniline | | 285 | 100·00 | |

The salt, therefore, corresponds to the common phosphate of soda:

$$2\,Na,\,H,\,PO_8,$$

and also to an ammonia salt of the same constitution.

It is anhydrous, like this ammonia salt; but, unlike the latter, possesses, as before remarked, an acid reaction, like all the other salts of aniline, this base being incapable of destroying the properties of an acid.

2. PHOSPHATE WITH 1 EQUIV. OF ANILINE AND 2 EQUIV. OF HYDROGEN.

This compound is obtained by adding tribasic phosphoric acid to the salt mentioned before until it ceases to produce a precipitate with chloride of barium, and concentrating in the water-bath. In the course of a few hours the salt crystallizes in beautiful silky needles; they are to be washed with ether and dried on a warm tile.

When dry the salt is quite white, but by exposure to the air becomes rose-red; it is very soluble in ether, alcohol, and water; in the latter with decomposition, the common phosphate being produced.

When burnt with protoxide of copper:

I. 0·456 grm. of substance gave:
0·633 „ „ carbonic acid, and
0·223 „ „ water.

II. 0·403 „ of substance, neutralized with ammonia and precipitated with nitrate of silver, gave:
0·880 „ of tribasic phosphate of silver.

These numbers correspond to the following per centage:

| | I. | II. |
|---|---|---|
| Carbon . . . . . | 37·86 | — |
| Hydrogen . . . . . | 5·44 | — |
| Phosphorus . . . . . | — | 37·12 |

leading to the formula:

$$H,\,C_{12}\,H_7\,N,\,2HO,\,PO_8,$$

as is seen by the following comparison:

| | | | Theory. | | Experiment. |
|---|---|---|---|---|---|
| 12 | equiv. | of Carbon . . . . . | 72 | 37·51 | 37·86 |
| 10 | „ | „ Hydrogen . . . . | 10 | 5·21 | 5·44 |
| 1 | „ | „ Nitrogen . . . . | 14 | 7·29 | — |
| 8 | „ | „ Oxygen . . . . . | 64 | 33·34 | — |
| 1 | „ | „ Phosphorus . . . | 32 | 16·66 | 16·61 |
| 1 | „ | „ Phosphate of Aniline | 192 | 100·00 | |

This salt corresponds to the biphosphate of soda,

$$Na, 2H, PO_8.$$

Mitscherlich has analysed an ammonia compound of the same constitution.

I did not succeed in forming a phosphate in which the three equivalents of hydrogen in the hydride are replaced by three equivalents of aniline. On adding aniline in excess to an alcoholic solution of common phosphate the base did not combine, the salt remaining unchanged. I also tried to produce it by decomposing the phosphate with three equivalents of soda by oxalate of aniline; aniline, however, was instantly set free in the form of oily globules, and the common phosphate was produced with oxalate of soda.

I have not been more successful in endeavouring to prepare phosphates, into which aniline enters beside fixed bases. I have tried to obtain a salt corresponding to phosphorus salt.

$$Na, NH_4, H, PO_8,$$

by dissolving aniline in a solution of phosphate of soda with one equivalent of fixed base. The crystals, however, which were formed did not contain soda, and were similar in appearance to the salt first-described. Similar results were obtained by neutralizing the acid phosphate of aniline with carbonate of soda. The salt produced did likewise not contain soda, the common phosphate appearing to be produced.

### II. PYROPHOSPHATE OF ANILINE.

There are two pyrophosphates of aniline, acid and neutral, which are always formed together when aniline is added in excess to pyrophosphoric acid. The precipitate produced by addition of aniline to pyrophosphoric acid is gelatinous, and becomes quite hard when exposed to the air.

Several combustions showed me that the compound obtained in this way consists of a mixture of the neutral and the acid pyrophos-

phate. I have not yet been able to obtain the neutral salt in a state of purity, but I found that by keeping the pyrophosphoric acid in great excess, the acid salt may be procured. The best way of forming it is to add aniline to rather concentrated pyrophosphoric acid (obtained by decomposing pyrophosphate of lead by hydrosulphuric acid), when the acid salt is precipitated along with the neutral compound; the mixture is then to be heated until the whole is dissolved, an excess of acid added, and the solution evaporated in the water-bath; upon cooling, the whole solidifies to a mass of beautiful white needles, which are to be pressed between bibulous paper, washed with ether, and finally dried *in vacuo*. This salt appears as white silky needles, very similar to the common basic sulphate of quinine; they are very acid, soluble in water, and almost insoluble in alcohol and ether; the crystals and their aqueous solution, like all other aniline salts, become red when exposed to the air.

When burnt with protoxide of copper:

I. 0·223 grm. of substance gave:
0·333 „ „ carbonic acid, and
0·117 „ „ water.

II. 0·269 „ of substance gave:
0·389 „ „ carbonic acid, and
0·132 „ „ water.

III. 0·350 „ of substance, neutralized by ammonia and precipitated by nitrate of silver, gave:
0·578 „ of pyrophosphate of silver.

These numbers correspond to the following per centage composition:

| | I. | II. | III. |
|---|---|---|---|
| Carbon . . . | 39·00 | 39·43 | — |
| Hydrogen . . | 5·68 | 5·45 | — |
| Phosphorus . . | — | — | 38·85 |

leading to the formula:

$$H, C_{12} H_7 N, H, PO_7,$$

as is seen by the following comparison:

| | | Theory. | | Experiment. |
|---|---|---|---|---|
| 12 equiv. of Carbon . . . . . | 72 | 39·34 | 39·22 |
| 9 „ „ Hydrogen . . . . . | 9 | 4·92 | 5·56 |
| 1 „ „ Nitrogen . . . . . | 14 | 7·05 | — |
| 7 „ „ Oxygen . . . . . | 56 | 30·61 | — |
| 1 „ „ Phosphorus . . . . . | 32 | 17·48 | 17·38 |
| 1 equiv. of Pyrophosphate of Aniline | 183 | 100·00 | |

This salt corresponds to the acid pyrophosphate of soda,

$$Na, H, PO_7,$$

analysed by Professor Graham.

An analogous salt of ammonia is not known; pyrophosphate of ammonia existing only in solution, which, according to Graham's experiments, yields, on evaporation, crystals of the common phosphate of ammonia, with 2 equivalents of the volatile alkali and 1 equivalent of water.

### III. METAPHOSPHATE OF ANILINE.

I obtained this salt by adding a great excess of aniline to a very strong solution of metaphosphoric acid (glacial acid perfectly pure), or by adding metaphosphoric acid to a solution of aniline in alcohol or ether; in both cases the salt precipitates as a gelatinous white mass; this is to be placed on a filter and well-washed with ether, until the excess of aniline is removed, and no smell of this body perceived, pressed and dried over sulphuric acid *in vacuo*.

When dry, the salt appears as an amorphous white mass, which changes rose-red in the air, becoming glutinous. It is acid to litmus paper, soluble in water, and almost insoluble in alcohol and ether.

Its solution dissolves metaphosphate of silver, which property belongs also to metaphosphate of soda; upon boiling, it changes red, and partly reduces the silver salt. When an aqueous solution is boiled for a long time, it is transformed into common phosphate of aniline.

When burnt with protoxide of copper:

I. 0·664 grm. of substance gave:
0·976 „ „ carbonic acid, and
0·264 „ „ water.

I determined the acid by precipitating with acetate of lead in great excess and boiling for a long time; the metaphosphate of lead is completely changed into the tribasic salt. This is a very advantageous method of determining metaphosphoric acid.

II. 0·5785 grm. of substance gave:
1·3485 „ of tribasic phosphate of lead.

These numbers correspond to the following per centage:

| | I. | II. |
|---|---|---|
| Carbon . . . . . | 41·33 | |
| Hydrogen . . . . | 4·55 | |
| Phosphorus . . . . | — | 18·34 |

These analyses lead to the formula:

$$H, C_{12} H_7 N, PO_6,$$

as is seen by the following:

| | | | Theory. | | Experiment. |
|---|---|---|---|---|---|
| 12 | equiv. | of Carbon . . . . . | 72 | 41·48 | 41·33 |
| 8 | „ | „ Hydrogen . . . . | 8 | 4·62 | 4·55 |
| 1 | „ | „ Nitrogen . . . . . | 14 | 8·11 | — |
| 6 | „ | „ Oxygen . . . . . | 48 | 27·58 | — |
| 1 | „ | „ Phosphorus . . . . | 32 | 18·39 | 18·34 |
| 1 equiv. of Metaphosphate of Aniline | | | 174 | 100·00 | |

This salt is analogous to Professor Graham's metaphosphate of soda:

$$Na\ PO_6,$$

which, according to the experiments of this chemist, likewise becomes viscid on evaporation, and never presents the slightest trace of crystallization.

The corresponding metaphosphate of ammonia is only known in solution. On evaporation this salt assimilates 1 equivalent of water, passing into the common phosphate with 1 equivalent of ammonia and 2 equivalents of water.

The experiments which I have described prove that there exist the following series of phosphates of aniline:

| | |
|---|---|
| Phosphates . . . . . | $\left\{\begin{array}{l} 2(H, C_{12} H_7 N), H, PO_8. \\ H, C_{12} H_7 N, 2H, PO_8. \end{array}\right.$ |
| Pyrophosphate . . . . | $H, C_{12} H_7 N, H, PO_7.$ |
| Metaphosphate . . . . | $H, C_{12} H_7 N, PO_6.$ |

This series embraces compounds corresponding to all the combinations of soda with phosphoric acid, except the phosphate with 3 equivalents of soda, and the pyrophosphate with 2 equivalents of fixed base.

The aniline salt, corresponding to the latter exists, however, but could as yet not be obtained in a state of purity.

All the compounds of aniline with phosphoric acid are anhydrous, like the other salts of this base, which have been examined by Professor Hofmann. In this respect they differ from the corresponding

soda salts, which nearly all contain a larger or smaller amount of water of crystallization. The two ammonia salts of phosphoric acid which we know, are, however, likewise anhydrous.

From the results of the preceding investigation, we may conclude that the organic bases comport themselves also with polybasic acids like mineral oxides. I intend, however, to analyse the phosphates of some other organic alkaloids, particularly of those which occur in nature, and are frequently employed in medicine.

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## XV.—*On Cumidine; a New Organic Base.*

By Edward Chambers Nicholson, Esq.

(Read before the Chemical Society of London, Nov. 1, 1847.)

The recognition of a close connection between the physical properties and chemical constitution of bodies, which has latterly attracted the attention of chemists, has chiefly been arrived at by comparing substances of corresponding series, which present a close and simple relation to each other. Our knowledge in this direction is, as yet, but limited, and certainly can only be extended by a careful comparison of the members of various parallel groups.

The beautiful relation, between the boiling point, and the number of equivalents of carbon and hydrogen of various compounds, which the researches of H. Kopp have pointed out, can only be verified and fully established by a still more complete investigation of analogous substances.

It was in consequence of these considerations that Dr. Hofmann occasioned a series of experiments to be carried on in his laboratory, on the derivatives of cuminic acid, a substance which the researches of Gerhardt and Cahours have proved to be an analogue of benzoic acid, the products from which latter substance have been more completely studied than those from any other body.

As a part of these researches, some of which have already been communicated to the Chemical Society, I had undertaken the study of the derivatives of cumol; the bodies corresponding to nitrobenzol, dinitrobenzol, azobenzol, aniline and nitraniline. None of these bodies were known when I commenced this investigation: some time since, however, M. Cahours gave notice in a paper, "On the action of a mixture of sulphuric and nitric acids on several organic substances," that he was engaged with an investigation of the same subject.

In this notice, M. Cahours gives the composition of nitrocumol and dinitrocumol, and briefly mentions that these bodies are converted into basic substances by the action of reducing agents.

In consequence of this announcement, I refrain from a further prosecution of this subject, and will give here only the results, which I have obtained, by examining the member, which in the cumol series, is the representative of aniline in the benzol series.

## PREPARATION OF CUMIDINE.

The preparation of this base from cumol is exactly analogous to that of aniline from benzol.

Cumol was treated with fuming nitric acid until it was entirely dissolved, heat being evolved during the reaction, and a large quantity of red vapours given off. On the addition of water, a dark red oily body precipitated, which was nitrocumol. An alcoholic solution of this substance was saturated first with ammoniacal gas, and then with hydrosulphuric acid. After the lapse of a few days, the liquid lost the smell of that gas, and a large quantity of sulphur separated; it was again treated with hydrosulphuric acid and distilled. This process was continued until the whole of the nitrocumol was decomposed. Alcohol and sulphide of ammonium having been removed by the last distillation, the residue in the retort was dissolved in hydrochloric acid, filtered from a small quantity of sulphur, and evaporated, until, upon cooling, the whole became a crystalline mass.

These crystals constituted the hydrochlorate of the representative in the cumol series, of aniline and toluidine in their respective series, and for which I propose the name of "Cumidine." On treating the boiling aqueous solution of this salt with caustic potassa, the base immediately separated in oily drops, which collected in an uniform layer, on the surface of the fluid. The purification of the base was very simple. The distillate was saturated with a concentrated solution of oxalic acid, and evaporated to dryness:—the residue dissolved in boiling alcohol, and treated with animal charcoal. On cooling, the oxalate was deposited in colourless crystalline plates, which were absolutely pure. The solution of this salt in water was decomposed by hydrate of potassa. On separating the oily liquid, by means of a pipette, and distilling rapidly, the base was obtained pure and colourless; traces of water having been previously removed by contact with potassa.

### COMPOSITION OF CUMIDINE.

The preparation and properties of this base, being analogous to those of aniline and toluidine, left no doubt in my mind as to its composition. Nevertheless, I have made the following determinations of carbon, hydrogen and nitrogen, which prove that cumidine, like the above-mentioned substances, is free from oxygen.

When burnt with protoxide of copper, the following results were obtained:

I. 0·2017 grm. of cumidine gave:
0·5902 „ „ carbonic acid, and
0·1755 „ „ water.
II. 0·4944 „ of substance gave:
45 c. c. of moist nitrogen. Bar. 768·9 mm. (30·27 in.) Therm. 18° C. (64°.5 F.)

which, calculated for 100 parts, give:

| | I. | II. |
|---|---|---|
| Carbon . . . . . | 79·82 | — |
| Hydrogen . . . . . | 9·66 | — |
| Nitrogen . . . . . | — | 10·67 |

agreeing exactly with the formula:

$$C_{18}\,H_{13}\,N,$$

as will be seen when the experimental numbers are placed in comparison with the calculated values:

| | | Theory. | | Experiment. |
|---|---|---|---|---|
| 18 equiv. of Carbon . . . . | 108 | 80·00 | | 79·82 |
| 13 „ „ Hydrogen . . . | 13 | 9·63 | | 9·66 |
| 1 „ „ Nitrogen . . . | 14 | 10·37 | | 10·67 |
| 1 „ „ Cumidine . . . | 135 | 100·00 | | 100·15 |

To prove the accuracy of the formula of this base, and control its atomic weight, I submitted the platinum double compound to a careful analysis. Two determinations, which I shall hereafter mention in detail, gave 28·85 and 28·93 per cent of platinum, the corresponding numbers to which closely agree with the calculated atomic weight.

| | | Mean. | Theory. |
|---|---|---|---|
| I. Atomic weight by experiment . | 135·82 | 135·32 | 135·00 |
| II. „ „ „ . | 134·82 | | |

The formation of cumidine from nitrocumol, is analogous to that of aniline and toluidine from nitrobenzol and nitrotoluol:

$$\underbrace{C_{18}\,H_{11}\,NO_4}_{\text{Nitrocumol.}} + 6\,HS = \underbrace{C_{18}\,H_{13}\,N}_{\text{Cumidine.}} + 4\,HO + 6\,S.$$

## PROPERTIES OF CUMIDINE.

This body, as previously stated, is obtained in the form of a slightly yellowish oil, dispersing and refracting light in an eminent degree, and possessing a peculiar smell and burning taste. In a mixture of ice and salt, it solidifies to a mass of square plates, which rapidly disappear when the temperature increases. It seems, that under peculiar circumstances, this body becomes crystalline at ordinary temperatures. On one occasion, in the winter, I obtained it in beautiful square plates, resembling those obtained when the oil is exposed to a frigorific mixture, and which have continued solid up to the present time. It is also well known that toluidine and napthalidine often remain liquid for a considerable period.

Cumidine is very soluble in alcohol, ether, pyroxilic spirit, bisulphide of carbon, and the fatty oils. Water also dissolves it in small quantity. The base has no action on reddened litmus or tumeric papers. It evaporates but slowly at ordinary temperatures, and leaves a stain on paper, which disappears after some time. Cumidine is lighter than water, its spec. grav. being 0·9526.

I was very anxious to ascertain the boiling point of cumidine:—in two experiments made with different specimens, the liquid boiling in contact with a coil of platinum wire, and nearly an ounce distilling over, the thermometer became stationary at 225° C. (437° F.) Bar. 761·1 mm. (29·965 in.)

On comparing this result with the number calculated by H. Kopp's empirical rule, a considerable discrepancy is obvious.

If we take, as a starting point, the boiling temperature of aniline, which has lately been verified in several experiments by Dr. Hofmann, we obtain the following calculated numbers, for the series of bases between aniline and cumidine:

| | | | |
|---|---|---|---|
| Aniline . . . | 182° C. | 182° C. | Hofmann. |
| Toluidine . . . | 201 „ | 198 „ | Muspratt & Hofmann. |
| Unknown base . | 220 „ | — „ | „ „ „ |
| Cumidine . . . | 239 „ | 225 „ | Nicholson. |

Cumidine, when recently distilled, is nearly colourless, but on a few minutes' exposure to the air, rapidly assumes, first a yellow, and

finally a dark red colour; this alteration takes place with greater rapidity at high temperatures. Its vapour is highly inflammable, burning with a yellowish flame, and depositing large quantities of carbon.

Cumidine, like aniline and toluidine, imparts an intense yellow colour to fir-wood, but it does not afford the beautiful reaction with hypochlorite of lime which characterizes the former base.

The basic properties of this substance, although very feeble, are rendered obvious by its comportment with the salts of weak mineral oxides. An aqueous solution of cumidine separates hydrated sesquioxide of iron from the sesquichloride, but gives no precipitate with the salts of zinc or alumina.

### COMPOUNDS OF CUMIDINE.

The basic character of this substance is, moreover, exhibited in the extraordinary facility with which it forms crystalline compounds with acids; a property in which it also resembles aniline and toluidine. All these salts, except some metallic double compounds, are colourless when recently prepared; but some of them, especially when moist, or exposed to a high temperature, assume a pinkish hue. They are soluble in water, and more so in alcohol. When decomposed by the caustic alkalies, the base separates in dark oily globules if the solution be concentrated; if dilute, as a white curdy precipitate. All the salts of cumidine, like those of aniline, are anhydrous. They are acid to litmus paper. When rapidly boiled in water for some time, they are partially decomposed, the base volatilising.

### SULPHATE OF CUMIDINE.

I obtained this salt by dissolving the base in boiling dilute sulphuric acid; upon cooling, the whole became a crystalline mass. When dissolved in water, and decolorised by animal charcoal, crystals of perfect purity were obtained on cooling.

This salt is only slightly soluble in water, but more so in alcohol; it is inodorous, but possesses a disagreeable bitter taste. At 100° C. (212° F.) it emits the odour of the base, but is not otherwise altered in properties, except that it assumes a faint pink tint.

I. 0·2357 grm. of substance, burnt with protoxide of copper, gave:
0·5070 „ „ carbonic acid, and
0·1687 „ „ water.

II. 0·2994 grm. of substance, precipitated with chloride of barium, gave:
0·1902 „ „ sulphate of barium, which quantity agrees with the following composition in 100 parts:

| | I. | II. |
|---|---|---|
| Carbon . . . . . | 58·66 | — |
| Hydrogen . . . . . | 7·94 | — |
| Sulphuric acid . . . . | — | 21·77 |

corresponding to the formula:

$$C_{18}\,H_{13}\,N,\,H\,SO_4,$$

as is seen by the following calculation:

| | | Theory. | | Experiment. |
|---|---|---|---|---|
| 18 equiv. of Carbon . . . . . | 108 | 58·70 | | 58·66 |
| 14 „ „ Hydrogen . . . . | 14 | 7·60 | | 7·94 |
| 1 „ „ Nitrogen . . . . . | 14 | 7·61 | | — |
| 1 „ „ Oxygen . . . . . | 8 | 4·35 | | — |
| 1 „ „ Sulphuric acid . . . | 40 | 21·74 | | 21·77 |
| 1 „ „ Sulphate of Cumidine. | 184 | 100·00 | | |

NITRATE OF CUMIDINE.

This salt is obtained by gently heating the base with dilute nitric acid. On cooling, the fluid becomes filled with long needle-like crystals, which are colourless, if the acid be not too concentrated, and are otherwise of a reddish tint.

It is soluble in water and alcohol, and is not decomposed at a temperature of 100° C. (212° F.)

I. 0·3231 grm. of substance, burnt with protoxide of copper, gave:
0·6460 „ „ carbonic acid, and
0·2145 „ „ of water,

which yield the following per centage:

| | |
|---|---|
| Carbon . . . . . | 54·52 |
| Hydrogen . . . . . | 7·37 |

agreeing with the formula:

$$C_{18}\,H_{13}\,N,\,H\,NO_6,$$

as is seen by the following calculation:

| | | Theory. | | Experiment. |
|---|---|---|---|---|
| 18 equiv. of | Carbon . . . . . | 108 | 54·54 | 54·52 |
| 14 „ | „ Hydrogen . . . . | 14 | 7·07 | 7·37 |
| 2 „ | „ Nitrogen . . . . . | 28 | 14.15 | — |
| 6 „ | „ Oxygen . . . . . | 48 | 24·24 | — |
| 1 equiv. of | Nitrate of Cumidine . | 198 | 100·00 | |

HYDROCHLORATE OF CUMIDINE.

The base combines directly with hydrochloric acid, with the evolution of heat. By re-crystallization from water or alcohol, the salt is obtained in large well-formed prisms, perfectly white and inodorous. If moist, or exposed to the air, it assumes a pink colour. It is not altered at a temperature of 100° C. (212° F.), but at a higher temperature it melts and sublimes.

I. 0·1810 grm. of substance, burnt with chromate of lead, gave:
0·4178 „ „ carbonic acid, and
0·1360 „ „ water.

II. 0·3908 „ „ substance, precipitated with nitrate of silver, gave:
0·3267 „ „ chloride of silver,

which, calculated for 100 parts, is equivalent to:

| | I. | II. |
|---|---|---|
| Carbon . . . . . | 62·94 | — |
| Hydrogen . . . . . | 8·34 | — |
| Chlorine . . . . . | — | 20·67 |

agreeing with the formula:

$$C_{18}\,H_{13}\,N,\,HCl,$$

as will be seen by a comparison with the following calculated numbers:

| | | Theory. | | Experiment. |
|---|---|---|---|---|
| 18 equiv. of | Carbon . . . . . | 108·0 | 62·97 | 62·94 |
| 14 „ | „ Hydrogen . . . . . | 14·0 | 8·17 | 8·34 |
| 1 „ | „ Nitrogen . . . . . | 14·0 | 8·17 | — |
| 1 „ | „ Chlorine . . . . . | 35·5 | 20·69 | 20·67 |
| 1 eq. of | Hydrochlorate of Cumidine . | 171·5 | 100·00 | |

Cumidine, when added to a boiling aqueous solution of oxalic acid, dissolves, and upon cooling, a salt crystallizes in beautiful pearly tables, which are difficultly soluble in water, but more so in alcohol.

I have made several analyses of this substance, and from the great difference in the numbers obtained, there remains no doubt that it is a mixture of the neutral with an acid oxalate. The small

amount of substance at my command, has prevented me from separating these two bodies in a state of purity.

### CUMIDINE AND BICHLORIDE OF PLATINUM.

This beautiful compound is obtained when an excess of bichloride of platinum is added to a hot solution of hydrochlorate of cumidine in water. Upon cooling, the compound is deposited in long yellow needles, which, after washing with a small quantity of water, are perfectly pure. This substance is decomposed when boiled with water. Its deportment with alcohol and ether is very singular. On adding a few drops of alcohol to a large quantity of this substance, it immediately dissolves, and after a short time, is precipitated in the form of a dark red oil, which, after evaporation of the alcohol, solidifies to a mass of crystals of a magnificent orange-yellow colour. At a temperature of 100° C. (212° F.) it becomes rather darker in colour, but is not otherwise altered in properties. At a higher temperature it is decomposed into hydrochlorate of cumidine, which sublimes, and metallic platinum.

I. 0·3468 grm. of substance, burnt with chromate of lead, gave:
0·3985 „ „ carbonic acid, and
0·1400 „ „ water.
II. 0·4793 „ „ substance gave:
0·1383 „ „ platinum.
III. 0·4967 „ „ substance gave:
0·1437 „ „ platinum,

which quantities agree with the following per centage composition:

| | I. | II. | III. |
|---|---|---|---|
| Carbon . . . . | 31·33 | — | — |
| Hydrogen . . . | 4·48 | — | — |
| Platinum . . . | — | 28·85 | 28·93 |

and with the formula:

$$C_{18}\,H_{13}\,N,\,HCl,\,Pt\,Cl_2,$$

as may be seen by the following calculation:

| | Theory. | | Experiment. |
|---|---|---|---|
| 18 equiv. of Carbon . . . . . | 108·00 | 31·65 | 31·33 |
| 14 „ „ Hydrogen . . . . | 14·00 | 4·12 | 4·48 |
| 1 „ „ Nitrogen . . . . | 14·00 | 4·12 | — |
| 3 „ „ Chlorine . . . . | 106·50 | 31·21 | — |
| 1 „ „ Platinum . . . . | 98·68 | 28·90 | 28·89 |
| 1 eq. of Bichloride of Platinum and Cumidine . . . . . | 341·18 | 100·00 | |

I have not examined the other salts of this base, and shall only remark, that the hydrobromate, hydriodate, hydrofluate, metaphosphate, phosphate, acetate and tartrate, are immediately produced, when these acids are brought into contact with anhydrous cumidine. The hydriodate of cumidine seems to be the most soluble of its compounds.

Besides the simple salts mentioned, cumidine forms a great number of double compounds.

Bichloride of palladium produces a yellow precipitate, very similar in appearance to the platinum salt; it is soluble in water and alcohol, and crystallizes from the latter solvent in yellow needles.

An alcoholic solution of this base produces a violet precipitate with sesquichloride of gold, rather darker in colour than ferrocyanide of copper. It is soluble in alcohol, to which it imparts an intense colour.

Nitrate of cumidine combines with nitrate of silver, and forms a beautiful compound, crystallizing in long needles, which are soluble in water and alcohol without decomposition.

An alcoholic solution of cumidine produces, with chloride of mercury, a white granular precipitate, which is decomposed by boiling water, with the formation of a yellow powder. With cyanide of mercury, cumidine also gives a crystalline precipitate.

Sulphate of copper produces a beautiful grass-green precipitate in an alcoholic solution of the base, which is insoluble in water and alcohol.

In the following table I subjoin the formulæ of the compounds analysed:

| | |
|---|---|
| Cumidine . . . . . | $C_{18}\,H_{13}\,N$, |
| Hydrochlorate of Cumidine | $C_{18}\,H_{13}\,N$, HCl |
| Sulphate of Cumidine . . | $C_{18}\,H_{13}\,N$, $H\,SO_4$ |
| Nitrate of Cumidine . . . | $C_{18}\,H_{13}\,N$, $H\,NO_6$ |
| Platinum-salt . . . . . | $C_{18}\,H_{13}\,N$, HCl, $PtCl_2$. |

### PRODUCTS OF THE DECOMPOSITION OF CUMIDINE.

The great number of changes which oil of cummin undergoes before its conversion into cumidine: the treatment of the oil with hydrate of potassa, in order to separate the cymol and to convert the cuminol into cuminic acid; the distillation of this acid with caustic lime, to procure cumol; the conversion of the cumol into nitrocumol, by fuming nitric acid; and finally, the reduction of nitrocumol by hydrosulphuric acid, render the preparation of this base, in any quantity, a long and laborious process. In consequence of this difficulty, I could but briefly study the products of its decomposition.

*Potassium*, when heated in the vapour of cumidine, is converted into cyanide of potassium.

Concentrated *nitric acid* dissolves the base with a beautiful purple colour. On adding water to the solution, a flocculent precipitate is produced, which partakes of the character of an acid.

Dry *chromic acid* acts very powerfully on cumidine; great heat is evolved, but the base does not inflame like aniline.

On treating cumidine with *bromine*, a violent action ensues, with the disengagement of heat and evolution of hydrobromic acid. The base is converted into a solid grey mass, which is soluble in alcohol and ether, but insoluble in water, and crystallizes from the former solvents in long white needles. The great analogy in the properties and in the mode of formation of this body to those of tribromaniline, render it very probable that it is tribromocumidine:

$$C_{18}\left\{\begin{matrix}H_{10}\\Br_3\end{matrix}\right\}N.$$

When treated with a mixture of *hydrochloric acid* and *chlorate of potassa*, the base is powerfully attacked and converted into a brown viscid mass, which has exactly the smell of chlorophenissic acid. When boiled in alcohol, it partially dissolves, and leaves a crystalline substance.

Aniline, when treated in a similar manner, yields, as is known, a mixture of chloranil and chlorophenissic acid; whether the products obtained in the decomposition of cumidine are identical with those of aniline, or whether they only represent these products in the cumol series, has to be decided by further experiments, which I soon hope to undertake.

Cumidine also produces a class of substances analogous to the amides and anilides.

The base, when exposed to an atmosphere of phosgene gas, immediately solidifies with the evolution of heat; when washed with water to free it from hydrochlorate of cumidine, and then dissolved in boiling alcohol, it deposits on cooling, large crystals, very similar in appearance to nitrate of potassa.

A mixture of bisulphide of carbon and cumidine, after the lapse of a few hours, evolves a large quantity of hydrosulphuric acid; upon the addition of water, an oily body separates, which soon solidifies to a crystalline mass. It is soluble in boiling alcohol, from which it is deposited in colourless needles.

These two latter substances are evidently carbo-cumidide and sulphocarbo-cumidide, corresponding to carbanilide and sulphocarbanilide, lately described by Dr. Hofmann.

Oxalate of cumidine, when submitted to dry distillation, yields a crystalline substance, which is but difficultly soluble in water, and shows in every respect the comportment of oxicumidide.

I have not made an analysis of these bodies, but there is little doubt that their composition may be represented by the following formulæ:

| | |
|---|---|
| Carbocumidide . . . . . | $C_{18} H_{12} N, C O$ |
| Sulphocarbocumidide . . . | $C_{18} H_{12} N, C S$ |
| Oxicumidide . . . . . | $C_{18} H_{12} N, C_2 O_2$. |

---

Messrs. Muspratt and Hofmann, in their paper on Toluidine, have proved that the formation of azobenzol, by the action of an alcoholic solution of hydrate of potassa on nitrobenzol, is always accompanied by a simultaneous production of aniline. I was anxious to ascertain whether nitrocumol would undergo an analogous metamorphosis.

On distilling an alcoholic solution of nitrocumol with caustic potassa, a violent reaction ensued, and a deep red-coloured oil collected in the receiver, which perfectly resembled azobenzol, before it had solidified; in the latter stage of the process, a large quantity of cumidine passed over; the residue in the retort contained considerable quantities of oxalate of potassa.

The formation of these substances is accompanied, and, as it seems, preceded by others; but the final reaction may be represented by the following equation:

$$2\,\underbrace{(C_{18} H_{11} NO_4)}_{\text{Nitrocumol.}} + \underbrace{HO, C_4 H_5 O}_{\text{Alcohol.}} = \underbrace{C_{18} H_{11} N}_{\text{Azocumol.}} + \underbrace{C_{18} H_{13} N}_{\text{Cumidine.}} + \underbrace{2\,(H, C_2 O_4)}_{\text{Oxalic acid.}} + 2\,HO.$$

These experiments have been carried on in the laboratory of the Royal College of Chemistry; and I cannot refrain from expressing my greatest thankfulness to Dr. Hofmann, for his superintendence and advice during their prosecution.

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## XVI.—*On some of the Products of Oxidation of Cumol by Nitric Acid.*

By Mr. F. A. Abel.

(Read before the Chemical Society of London, June 21st, 1847).

From the investigations on the action of nitric acid upon organic bodies, *one* result, in reference to the manner in which this acid acts, has been undoubtedly established. We know that in most cases the carbon of the organic substance remains untouched; that according to the degree of concentration of the acid a smaller or larger number of equivalents of hydrogen are expelled, and that the remaining part of the organic body combines with the remainder of the nitric acid. Thus is produced that innumerable class of neutral compounds considered by some chemists to be combinations of nitrous acid with organic oxides, and by others to be products of the substitution of hyponitric acid for hydrogen. It is indifferent which of these views is adopted, the fact having been established by hundreds of experiments, and we are enabled by analogy to predict with tolerable certainty the result of any new experiment.

The case is quite different when the oxidation is not confined to the hydrogen, but is extended to the carbon. The numerous experiments made on this subject do not as yet afford any general conclusion; we are far from being able to form an opinion, previous to experiment, of the nature of the product formed. This will be obvious if we examine the action of nitric acid on a class of bodies which are very nearly related to each other, both by the manner in which they are formed and in their general chemical behaviour. Benzol, toluol, cinnamol (styrol), cumol, napthalol, cymol, are acted upon by nitric acid, the corresponding products of substitution being formed.

| | | | | | |
|---|---|---|---|---|---|
| Benzol . . | $C_{12}H_6$ | Nitrobenzol . . . | $C_{12}\left\{\begin{matrix}H_5\\NO_4\end{matrix}\right\}$ | Dinitrobenzol . . | $C_{12}\left\{\begin{matrix}H_4\\2NO_4\end{matrix}\right\}$ |
| Toluol . . | $C_{14}H_8$ | Nitrotoluol . . . | $C_{14}\left\{\begin{matrix}H_7\\NO_4\end{matrix}\right\}$ | Dinitrotoluol . . | $C_{12}\left\{\begin{matrix}H_6\\2NO_4\end{matrix}\right\}$ |
| Cinnamol . | $C_{16}H_8$ | Nitrocinnamol . . | $C_{16}\left\{\begin{matrix}H_7\\NO_4\end{matrix}\right\}$ | | |
| Cumol . . | $C_{18}H_{12}$ | Nitrocumol . . . | $C_{18}\left\{\begin{matrix}H_{11}\\NO_4\end{matrix}\right\}$ | Dinitrocumol . . | $C_{18}\left\{\begin{matrix}H_{10}\\2NO_4\end{matrix}\right\}$ |
| Naphthalol . | $C_{20}H_8$ | Nitronaphthalol . | $C_{20}\left\{\begin{matrix}H_7\\NO_4\end{matrix}\right\}$ | Dinitronaphthalol | $C_{20}\left\{\begin{matrix}H_6\\2NO_4\end{matrix}\right\}$ |
| Cymol . . | $C_{20}H_{14}$ | Nitrocymol . . . | $C_{20}\left\{\begin{matrix}H_{13}\\NO_4\end{matrix}\right\}$ * | | |

* This substance is now under investigation by Mr. Noad.—Dr. A. W. H.

In the above two columns of combinations, the number of equivalents of carbon will be found the same as in the carbo-hydrogens. We have, however, with most of these bodies, either by continued action of nitric acid upon them, or by the observation of particular conditions, succeeded in oxidizing also a portion of their carbon; bodies of acid properties being thus produced, which contain a smaller number of equivalents of carbon than the carbo-hydrogens from which they are derived. The composition of these acids does not, however, bear any constant relation to the carbo-hydrogens, as it does in the above-mentioned products of substitution.

By the continued action of nitric acid on naphthalol, naphthalic acid, discovered by Laurent and Marignac,* is produced, the composition of which is expressed by the formula:

$$2\,H,\ C_{16}\,H_4\,O_8.$$

The action of nitric acid on cinnamol (styrol) has been studied by Drs. Hofmann and Blyth.† They have shown that cinnamol may in this manner be converted into benzoic acid.

The products obtained by the action of nitric acid on toluol have been studied by Deville.‡ He found that the two above-mentioned products of substitution were easily formed. He, moreover, believes to have converted toluol, by a long treatment with oxidizing agents, into benzoic acid; he is, however, in doubt about the result of his experiment, as he could not always succeed in the transformation, and his method of preparing toluol did not exclude the possibility of its containing benzoic ether in admixture. If benzoic acid can in reality be obtained from toluol, we have here an instance of the formation of an acid without the original number of equivalents of carbon in the carbo-hydrogen being diminished.

In a paper lately read before the Society, Mr. Noad has shown that by the continued action of dilute nitric acid, cymol is converted into toluylic acid.

It will be seen from these examples that we are unable to determine anything beforehand regarding the nature of these products of oxidation. The manner in which nitric acid or any other oxidizing agent acts is evidently closely connected with the constitution of the body exposed to their influence. Aided by the comportment of nitric acid with naphthalol, Marignac has in fact founded a view of the constitution of this body. He considers the carbo-

* Liebig's Annalen, XLI, p. 98, and XLII, p. 215.

† Trans. of Chem. Soc. vol. II, p. 334.

‡ Ann. de Chim. et de Phys. 3e sér. t. III, p. 168.

hydrogen in question to be a combination of two others, namely, $C_{16}\,H_4 + C_4\,H_4 = C_{20}\,H_8$, naphthalic acid, $C_{16}\,H_4\,O_6$, being formed by the action of nitric acid on the first, while the other is converted by the influence of the oxygen into water and oxalic or carbonic acid. By this view many of the reactions of naphthalol may be explained in a very satisfactory manner. It is possible that similar views may be applied to the other carbo-hydrogens, by which their behaviour with oxidizing agents will be similarly explained; a great number of investigations are, however, required before we can arrive at any general result.

The following experiments, which I have instituted at the suggestion and under the direction of Dr. Hofmann, may, I hope, be considered as a slight contribution to this subject.

It is known that when cumol is treated with concentrated nitric acid, it yields the usual products of substitution of the carbo-hydrogens. Gerhardt and Cahours have further observed, that by the continuous action of dilute nitric acid on cumol, a crystalline acid is produced.* This acid has not, however, been more closely investigated. According to the experiments on toluol, cinnamol and cymol before mentioned, this acid might be of three different kinds, according to the analogy of cumol with any one of these three carbo-hydrogens. If the number of equivalents of carbon were to remain the same as in toluol, the acid obtained might be $H\,C_{18}\,H_9\,O_4$, until now unknown (differing from toluylic and cuminic acid in containing $C_2\,H_2$, more and less). Should two equivalents of carbon be eliminated, as is the case with cinnamol, the formation of toluylic acid might then be expected; and lastly, should cumol be analogous to cymol, that is, should it lose four equivalents of carbon, the acid must then be benzoic acid.

In the preparation of cumol, I proceeded in the manner described by its discoverers, Gerhardt and Cahours. Pure cuminic acid was distilled with four times its weight of caustic lime in a copper retort placed in a deep sand-bath, the temperature of which was gradually raised to a red heat. The distillate obtained was colourless, possessing however an empyreumatic odour, which it did not lose on being rectified over hydrate of potassa to free it from any cuminic acid that might have come over with it. I afterwards found that this peculiar odour was immediately removed on distilling the oil with a concentrated solution of chromic acid, without its composition being at all affected. This is a method that might perhaps prove useful in many

* Liebig's Annalen, xxxviii, p. 67.

cases in which the peculiar odour of a carbo-hydrogen is disguised by the presence of a small quantity of some foreign substance.

When dried, over chloride of calcium, this body possessed exactly the same properties as described by Gerhardt and Cahours. Its boiling-point was found by them to be 144° C; a later experiment of Gerhardt gave 153° as the boiling-point. The cumol that I prepared boiled at 148° C. Its analysis gave me the following results:

0·2029 grm. of substance, burnt with protoxide of copper, yielded:
0·6725 „ „ carbonic acid, and
0·1804 „ „ water.

Corresponding to:

| | |
|---|---|
| Carbon . . . . . | 90·34 |
| Hydrogen . . . . . | 9·88 |

which numbers agree with the composition of cumol.

| | Theory. | | Experiment. |
|---|---|---|---|
| 18 equiv. of Carbon . . . . | 108 | 90 | 90·34 |
| 12 „ „ Hydrogen . . . | 12 | 10 | 9·88 |
| 1 equiv. of Cumol . . . . | 120 | 100 | 100·22 |

On boiling cumol with concentrated nitric acid it is quickly converted into a heavy oil, which is the analogue to nitrobenzol. If the boiling is continued, this oil disappears, and is gradually converted into a yellow crystalline mass, soluble in ammonia with the exception of a slight fixed residue (dinitrocumol). The ammoniacal solution gives with hydrochloric acid a white precipitate, difficultly soluble in cold water, but more easily so in hot water, from which it crystallizes on cooling. These crystals are generally somewhat coloured; recrystallization after treatment with animal charcoal removes this colouring matter.

Several combustions of the acid, dried at 100° C., showed me that my substance must be a mixture. I, therefore, distilled another portion of cumol with fuming nitric acid for several days, and obtained a crystalline body similar to the former, which was purified in the usual manner. A combustion of this substance gave me the following results:

0·2628 grm. of substance yielded:
0·4890 „ „ carbonic acid, and
0·0743 „ „ water.

Per centage composition:

| | |
|---|---|
| Carbon . . . . . | 50·73 |
| Hydrogen . . . . . | 3·18 |

These numbers correspond to the composition of nitrobenzoic acid:

$$H\,C_{14}\left\{\begin{matrix}H_4\\NO_4\end{matrix}\right\}O_4$$

as is seen when compared with the theoretical numbers:

| | | Theory. | Experiment. |
|---|---|---|---|
| 14 equiv. of Carbon . . . | 84 | 50·30 | 50·73 |
| 5 „ „ Hydrogen . . | 5 | 3·00 | 3·18 |
| 1 „ „ Nitrogen . . | 14 | 8·38 | — |
| 8 „ „ Oxygen . . . | 64 | 38·32 | — |
| 1 eq. of Nitrobenzoic Acid . | 167 | 100·00 | |

On addition of nitrate of silver to the ammoniacal salt of this acid a white precipitate was formed, sparingly soluble in hot water, from which it crystallized on cooling. I had not sufficient substance to recrystallize the salt, and could therefore only purify it by washing.

Its analysis gave me the following result:

0·1657 grm. of substance left, on being burnt,
0·0650 „ „ 39·24 per cent. of silver,

which agrees sufficiently well with the composition of nitrobenzoate of silver:

| | | Theory. | Experiment. |
|---|---|---|---|
| 1 eq. of Silver . . . . . | 108 | 39·41 | 39·21 |
| 1 „ „ Anhydride of Nitrobenzoic Acid | 166 | 60·59 | — |
| 1 eq. of Silver-salt . . . . . | 274 | 100·00 | |

In order to be perfectly certain, the small quantity remaining of the silver salt was submitted to distillation. There sublimed a portion of the acid, mixed with a few drops of an aromatic oil. The product of the distillation was now submitted to Dr. Hofmann's process for detecting nitrobenzol; it was dissolved for this purpose in a mixture of alcohol and sulphuric acid, and reduced by means of a piece of metallic zinc. After the disengagement of hydrogen had ceased, the liquid was neutralized with potassa and agitated with ether. A few drops of the ethereal solution gave, on evaporation with hypochlorite of lime, the beautiful violet colour characterizing aniline.

These experiments were sufficient to identify nitrobenzoic acid, and it seemed more than probable that the excess of carbonic acid obtained, in the first analysis, arose from the presence of benzoic acid.

I, therefore, distilled a fresh quantity of cumol with nitric acid, and recollecting the difficulty which Mr. Noad experienced in the preparation of toluylic acid, I employed my acid so dilute, that even on boiling the mixture no disengagement of red fumes was visible. Having continued the distillation for four or five days, the cumol was converted into a crystalline mass, which was drained off from the mother-liquor and recrystallized from water. The properties of this acid distinguished it immediately from nitrobenzoic acid; it was much more soluble in cold and hot water, and was easily recognized as benzoic acid. Not having sufficient substance for a combustion, I converted the acid into an ammoniacal salt, and precipitated the solution with nitrate of silver. A white flocculent precipitate was obtained, much more soluble in water than nitrobenzoate of silver. On cooling, beautiful crystals separated, having all the properties of benzoate of silver.

The analysis of this salt gave me the following results:

I. 0·1837 grm. of substance yielded:
0·1138 „ „ chloride of silver, corresponding to
0·0857 „ or 46·65 per cent. of silver.
II. 0·1658 „ yielded:
0·0780 „ or 47·04 per cent. of silver, which numbers correspond with the formula:

$$Ag\ C_{14}\ H_5\ O_4,$$

as may be seen when compared with the theoretical numbers:

| | Theory. | | Experiment. |
|---|---|---|---|
| 1 equiv. of Silver . . . . . | 108 | 47·16 | 46·84 |
| 1 „ „ Anhydride of Benzoic Acid | 121 | 52·84 | — |
| 1 equiv. of Benzoate of Silver . . . | 229 | 100·00 | |

This result is sufficiently near, considering the small amount of substance employed.

From these experiments we see that cumol, on being boiled continuously with nitric acid, is converted into benzoic and nitrobenzoic acids. The oxidation of cumol is, therefore, analogous to that of cymol.

$$\underbrace{C_{20}\,H_{14}}_{\text{Cymol.}} + 18\,O = \underbrace{H\,C_{16}\,H_7\,O_4}_{\text{Toluylic acid.}} + 4CO_2 + 6HO.$$

$$\underbrace{C_{18}\,H_{12}}_{\text{Cumol.}} + 18\,O = \underbrace{H\,C_{14}\,H_5\,O_4}_{\text{Benzoic acid.}} + 4CO_2 + 6HO.$$

The behaviour of cumol under the influence of the continued action of dilute nitric acid induced me to submit benzol, so nearly related to cumol, to a similar treatment. After having, however, continued the distillation for about a week, I could not obtain an acid from benzol. On employing even highly diluted acid, the benzol was gradually converted into nitrobenzol.

Neither benzol nor nitrobenzol is attacked by pure chromic acid, or the oxidizing mixture of bichromate of potassa and sulphuric acid. Results quite as unsatisfactory were obtained on boiling a solution of hyposulphobenzolic acid with chromic acid or binoxide of manganese.

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## XVII.—*On the Products of the Decomposition of Cuminate of Ammonia by Heat.*

By Frederick Field, Esq.

(Read before the Chemical Society of London, June 7, 1847.)

The peculiar mode of decomposition which the ammonia salts of inorganic acids exhibit, when exposed to the action of heat, occurs likewise in the ammonia compounds of organic acids, although the results in the latter instances are usually of a more complicated nature. In most of these cases a formation of water takes place, the hydrogen of which is derived from the volatile alkali, while the acid furnishes the oxygen, the residue combining in a more intimate manner with the nitrogen of the ammonia. In decompositions, however, of *inorganic* compounds this reduction seems to be carried at once as far as it can go, the whole of the hydrogen contained in the ammonia being converted into water; while in *organic* salts this hydrogen is eliminated only by degrees, an intermediate body being produced between the original ammonia salt and the final product of the decomposition. Thus we find that nitrite and nitrate of ammonia, when exposed to heat, are at once respectively converted into water, nitrogen, and nitrous oxide. Oxalate of ammonia, on the other hand, if submitted to a

gentle heat, loses only two equivalents of water, the residue of both base and acid combining to form oxamide, and only by a strong and brisk application of heat, Döbereiner converted it into cyanogen; the rest of the hydrogen being eliminated in the form of water.

The dry distillation of oxalate of ammonia thus affords the prototypes of two series of compounds, which may arise from ammoniacal salts by the elimination of two or four equivalents of water respectively. There are few cases, however, in which the decomposition of ammoniacal salts have been carefully studied, and the instances in which we are acquainted with the representative of the two types are exceedingly scarce. We are indeed intimate with a very great number of amidogen compounds analogous to oxamide (fumaramide, salicylamide, succinamide, anisylamide, &c.), but only a few of these have been obtained from ammoniacal salts by the action of heat. The greatest number of these bodies were produced by the change most compound ethers suffer under the influence of ammonia, a beautiful mode of decomposition first pointed out by Professor Liebig in the transformation of oxalate of ethyl into oxamide, or by the action of gaseous ammonia on other substances related in some manner with the acid: thus was chloride of benzoyle converted into benzamide by Wöhler and Liebig, and lately lactide into lactamide by Pelouze.

As yet, however, the members of the second class, those compounds standing to other acids in the same relation as cyanogen to oxalic acid, are very rare. From a beautiful experiment of Pelouze, we know that the vapour of formiate of ammonia, when passed through a red-hot tube, is converted into water and hydrocyanic acid. In their investigation on the radical of benzoic acid, Wöhler and Liebig obtained a peculiar oil by the action of heat on benzamide, which at that time they did not study more closely. The same body was at a later period obtained in the dry distillation of benzoate of ammonia, and fully examined by Fehling, who found that this interesting substance, to which he gave the name *benzonitrile*, has the composition

$$C_{14} H_5 N,$$

and is produced from benzoate of ammonia, exactly in the same manner as cyanogen and prussic acid are formed respectively from oxalate or formiate of ammonia. These facts did not long remain isolated. Schlieper, in an excellent examination he has lately published on the products of oxidation of gelatine by chromic

acid, discovered that in these reactions, among other products, the body

$$C_{10} H_9 N$$

is formed, valeronitryle or valerianate of ammonia,—4 equivs. of water.

The members of this class acquire every day a greater degree of importance. A remarkable paper, read before the Chemical Society a short time since by Dr. Kolbe and Mr. Frankland, has indeed opened a most interesting connexion between these bodies and another class of substances, which hitherto have been obtained by very different processes. The conversion of cyanide of ethyl into metacetonic acid by means of alkalies and acids, seems to indicate that cyanide of ethyl is nothing else than metacetonitryle. This experiment is likely to be of great importance, for it is exceedingly probable that the whole class of substances alluded to must be considered as a class of cyanogen compounds. It is evident that similar considerations may be applied to cyanide of methyl and cyanide of amyl, lately described by Balard; and the conversion of these cyanides respectively into acetic and caproic acids, which we have a right to anticipate on treating them with alkalies or acids, will prove that these compounds are the nitriles of acetic and caproic acids—acetonitryle and capronitryle—which as yet have not been obtained by the action of heat on the ammoniacal salts of these acids.

The following experiments on the action of heat on cuminate of ammonia have been made with the hope of contributing to the history of the nitryles, or organic cyanides, as they perhaps should be more correctly designated.

The cuminic acid, employed in my experiments, was prepared by the action of solid hydrate of potassa on oil of cumin, and the product perfectly freed from the least traces of cymol which it might possibly contain by precipitating the potassa salt by hydrochloric acid, dissolving the precipitated cuminic acid in ammonia, reprecipitating by hydrochloric acid, and crystallizing from water. The acid was then dissolved in strong ammonia, and the solution subjected to heat. The first portions which passed over, although consisting chiefly of water and ammonia, together with cuminate of ammonia, which is always carried over with the steam, presented more or less an opalescent appearance, indicative of traces of the oil. On evaporating the solution in the retort to dryness, a portion of the salt is decomposed, ammonia is evolved, and cuminic acid condenses in beautiful plates upon the sides and neck of the retort, separation going on even on raising the temperature; but

simultaneously another decomposition takes place, water is eliminated, in consequence of which there are produced a peculiar white crystalline body, difficultly soluble in water, and subsequently a colourless oil of a most fragrant odour; although the operation may seem very simple, experience alone teaches the proper regulation of temperature necessary to obtain these two bodies.

*Cuminamide.*—Observing, in my first experiments, evolution of ammonia and sublimation of cuminic acid on heating cuminate of ammonia, I thought that by heating it under pressure, the ammonia then not being able to escape, the desired change might be effected. Accordingly a portion of the salt was placed in a strong glass tube, and after sealing the other end, gradually heated in an oil-bath to nearly the boiling-point of the oil, and allowed to cool. On cooling, the mass appeared to have been completely fused, but perfectly solid and of a highly-crystallized texture. On examination, it was found to be insoluble in cold water and ammonia, but very soluble in hot water, from which it solidified into a crystalline mass as the temperature cooled; this alone sufficiently indicated that a complete change had been effected, the cuminate of ammonia being readily soluble in cold water. In order to ascertain the nature of the change, the product was dissolved in hot water, weak ammonia being added to dissolve any cuminic acid that might be mixed with it, and crystallized; the crystals were separated by filtration, and once more dissolved in a boiling dilute solution of ammonia, from which they separated on cooling in brilliant white crystalline plates, similar in appearance to benzamide. These were dried at 100° C. in a water-bath, and analysed in the usual manner.

I. 0·1740 grm. of substance gave:
   0·4700 „ „ carbonic acid, and
   0·1280 „ „ water.
II. 0·2480 „ yielded:
   0·6700 „ of carbonic acid, and
   0·1810 „ „ water.
III. In estimating the nitrogen:
   0·2870 grm. yielded:
   0·3900 „ of bichloride of platinum and ammonium.*

From these analytical results, the following per centages are obtained:

* In this operation a large quantity of an oily body is produced, which floats on the surface of the hydrochloric acid. It is evidently *cumol*.

| | I. | II. | III. |
|---|---|---|---|
| Carbon . | 73·66 | 73·67 | — |
| Hydrogen | 8·17 | 8·10 | — |
| Nitrogen . | — | — | 8·50 |

leading to the formula:

$$C_{20}\,H_{13}\,N\,O_2,$$

as may be seen from the following comparison of the theoretical and experimental numbers:

| | Theory. | | Experiment. |
|---|---|---|---|
| 20 equiv. of Carbon . . | 120 | 73·68 | 73·66 |
| 13 „ „ Hydrogen . . | 13 | 7·99 | 8·13 |
| 1 „ „ Nitrogen . . | 14 | 8.52 | 8·50 |
| 2 „ „ Oxygen . . | 16 | 9·81 | — |
| 1 equiv. of Cuminamide . | 163 | 100·00 | |

This body, therefore, is cuminamide:

$$NH_2,\,C_{20}\,H_{11}\,O_2,$$

having precisely the same relation to cuminate of ammonia as oxamide has to oxalate of ammonia.

In preparing large quantities of this substance, the employment of close tubes would have been very inconvenient; indeed I soon found that it can be obtained in a retort by the continued application of a heat sufficient to keep the salt in a state of semi-fluidity. The analyses II. and III. were made with a product obtained in this manner.

Cuminamide crystallizes like benzamide, in two forms, according to the nature of the solution; if crystallized rapidly, or from a strong solution, it separates in the form of crystalline tables of great brilliancy, but if the solution be dilute, it crystallizes after the lapse of some hours in long opaque needles, both forms having exactly the same composition. It is soluble in hot and cold alcohol in any proportion, as also in ether. This new amide differs from most others, that have been described, in remaining intact on the addition of a strong solution of potassa, or mineral acids: from the former it crystallizes in large plates after some days. Long boiling with acids or alkalies is scarcely sufficient to produce the characteristic conversion of amides, either into ammoniacal salts or combinations of the base with the acid and evolution of ammonia.

*Cumonitrile.*—On heating cuminate of ammonia until it is perfectly fused, and keeping the fused mass in a state of brisk ebullition, large

globules of a light yellowish oil passed over along with water, evidently derived from the decomposition of the salt; when the globules began to diminish, the process was interrupted, the oil was separated from the water in the receiver by means of a pipette, the remaining distillate added to the mass in the retort, and the process repeated as before; in this manner, after some half-dozen distillations, nearly an ounce of oil was obtained; it was well washed with ammonia to remove cuminic acid, which seemed to be soluble in the oil, then treated with hydrochloric acid to separate ammonia, thoroughly washed with water, and digested with chloride of calcium; after standing some days, it was distilled to separate the chloride of calcium, and carefully rectified, the first portions being rejected, as possibly containing traces of water; the middle portion was reserved and heated in a retort with a coil of platinum; the liquid entered into ebullition at 239° C., at which point it remained stationary, while at least a quarter of an ounce was passing over. This portion was employed in the following analyses:

I. 0·2120 grm. burnt with protoxide of copper, yielded:
0·6440 „ of carbonic acid, and
0·1450 „ „ water.
II. 0·2250 „ yielded:
0·6835 „ of carbonic acid, and
0·1610 „ „ water.
III. 0·2440 „ „ ignited with soda-lime, yielded:
0·3640 „ „ bichloride of platinum and ammonium.*

From these analytical results, the following per centages are obtained:

| | I. | II. | III. |
|---|---|---|---|
| Carbon . . . | 82·82 | 82·84 | — |
| Hydrogen . . | 7·59 | 7·96 | — |
| Nitrogen . . | — | — | 9·34 |

leading to the formula:

$$C_{20}\,H_{11}\,N,$$

as may be seen from the following comparison of the theoretical and experimental numbers:

* Professor Fehling found it difficult to estimate the nitrogen in benzonitrile in the form of ammonia, drops of oil passing over into the hydrochloric acid. In the case of cumonitrile, this method gave very accurate results; oily drops likewise passed over, but were evidently *cumol*.

| | | Theory. | Experiment. |
|---|---|---|---|
| 20 equiv. of Carbon . . | 120 | 82·76 | 82·83 |
| 11 „ „ Hydrogen . | 11 | 7·58 | 7·77 |
| 1 „ „ Nitrogen . . | 14 | 9·66 | 9·34 |
| 1 equiv. of Cumonitrile . | 145 | 100·00 | 99·94 |

This body is, therefore, cumonitrile,

$$C_{20}\,H_{11}\,N,$$

standing in the same relation to cuminate of ammonia as cyanogen does to oxalate of ammonia.

Cumonitrile is a perfectly clear and colourless liquid, possessing a high refractive power; it has a most powerful and agreeable odour and a burning taste; it is somewhat soluble in water, causing a turbidity in that liquid; it is soluble in all proportions in alcohol and ether; it is lighter than water, having a specific gravity 0·765 at 14° C. (57° Fahr.) The boiling-point, when in contact with metal, is constant at 239° C. (462·2° Fahr.), at the barometric pressure 0·7585 m. (29·85 inches). The equivalent of cuminic acid containing $3C_2\,H_2$ more than the equivalent of benzoic acid, it was interesting to compare the boiling-points of benzonitrile and cumonitrile. According to Fehling's experiments, the boiling-point of benzonitrile is 191° C.; on calculating from this observation the boiling-point of cumonitrile according to the rule first pointed out by H. Kopp, the boiling-point should be 191 + 3·19 = 248. Dr. Fehling does not, however, mention that he has had this substance boiling in contact with metal, and it is not improbable that the true boiling-point of benzonitrile is somewhat lower; the vapour of cumonitrile is very inflammable and burns with a bright flame, which deposits much carbon.

The strongest nitric acid has but little action upon this substance; after boiling, however, and setting aside for some days, crystals of cuminic acid are formed. On being heated with potassium, it darkens and apparently another oil is produced; the mass when washed and tested for cyanogen in the usual manner, gives a copious precipitate of prussian blue, which seems to be strongly in favour of the view which Kolbe and Frankland have recently promulgated. A strong alcoholic solution of potassa has no immediate action on cumonitrile, but after a day or two, on pouring the liquid into a watch-glass, it partially solidified into a yellow crystalline mass, a mixture of the original substance with white crystals. These crystals, after purification, had all the appearance of cuminamide; in

order to be sure, however, of this composition, they were burnt with protoxide of copper:

0·1740 grm. of substance gave:
0·4720 „ „ carbonic acid, and
0·1240 „ „ water,

the per centage of carbon and hydrogen calculated from these numbers being:

Carbon . . 73·62
Hydrogen . 7·91

corresponding to those of cuminamide, as may be seen by a comparison with the former analyses.

It appears then that cumonitrile, on the addition of potassa, is not, as might have been expected, converted into cuminate of ammonia, but into cuminamide, taking 2 instead of 4 equivalents of water:

$$C_{20}\,H_{11}\,N + 2HO = C_{20}\,H_{13}\,N\,O_2,$$

the latter body being, as before remarked, only slightly affected by alkalies or acids.

Having obtained one amide with comparative ease, several other ammoniacal salts were heated for the purpose of preparing analogous amidogen compounds. *Benzoate of ammonia* was tried unsuccessfully, and it appears from the account published by Fehling of his investigation of benzonitrile, that the residue in the retort consisted entirely of benzoate of ammonia, that salt appearing to have lost 4 equivs. of water without undergoing an intermediate conversion into an amide by the loss of 2 equivs. *Nitrobenzoic acid* was dissolved in ammonia, evaporated and cautiously fused for a considerable time; when cold it was found to be insoluble in water and ammonia at the ordinary temperature, but dissolved by hot water, from which it crystallized in beautiful yellow needles. On analysis, the following results were obtained:

I. 0·2220 grm. of substance, burnt with protoxide of copper, gave:
0·4100 „ „ carbonic acid, and
0·0800 „ „ water.
II. 0·2550 „ „ gave:
0·4720 „ „ carbonic acid, and
0·0870 „ „ water.

From these results the following per centages were obtained:

| | I. | II. |
|---|---|---|
| Carbon . . . | 50·36 | 50·43 |
| Hydrogen . . | 4·00 | 3·78 |

corresponding to the formula:

$$C_{14}\,H_6\,N_2\,O_6,$$

as may be seen from a comparison of the theoretical and experimental numbers:

| | Theory. | | Experiment. |
|---|---|---|---|
| 14 equiv. of Carbon . . . | 84 | 50·60 | 50·39 |
| 6 „ „ Hydrogen . . | 6 | 3·62 | 3·98 |
| 2 „ „ Nitrogen . . | 28 | 16·87 | — |
| 6 „ „ Oxygen . . . | 48 | 28·91 | — |
| 1 equiv. of Nitrobenzamide | 166 | 100·00 | |

This body is, therefore, nitrobenzamide, having the same relation to nitrobenzoate of ammonia as cuminamide has to cuminate of ammonia.

This beautiful substance can only be obtained with difficulty, as the nitrobenzoate of ammonia explodes violently unless very great caution is employed.

A specimen of chlorobenzoic acid, made in the laboratory for some other investigation, was dissolved in ammonia and heated; it fused readily, became perfectly insoluble in cold water and ammonia, but soluble in hot water, crystallizing as the solution cooled in long needles of great beauty. The specimen of acid afforded me, being all that could be spared, was insufficient for the manufacture of an amide; I, therefore, prepared a portion of chlorobenzoic acid by acting upon benzoic acid for some days with hydrochloric acid and chlorate of potassa; after purification it was burnt with chromate of lead and gave the following results:

0·3940 grm. of substance gave:
0·7690 „ „ carbonic acid, and
0·1140 „ „ water.

From this result the following per centage was obtained:

| | Theory. | Experiment. |
|---|---|---|
| Carbon . . . | 53·22 | 53·61 |
| Hydrogen . . | 3·22 | 3·25 |

leading to the formula:

$$H\,C_{14}\left\{\begin{matrix}H_4\\Cl\end{matrix}\right\}O_4.$$

This is benzoic acid, in which 1 equiv. of the hydrogen is replaced by 1 equiv. of chlorine.

This acid, however, on being subjected to the usual treatment with ammonia, and subsequently to the action of heat, did not fuse but blackened, charcoal being separated. Unfortunately the specimen of ammoniacal salt, from which I made the former compound, was not analysed, probably it would have proved to be:

$$H\,C_{14}\left\{\begin{matrix}H_3\\Cl_2\end{matrix}\right\}O_4,\text{ or }H\,C_{14}\left\{\begin{matrix}H_2\\Cl_3\end{matrix}\right\}O_4,$$

dichlorobenzoic or trichlorobenzoic acid, compounds, which according to the experiments of Dr. Stenhouse, are actually existing.

These experiments were conducted in the laboratory of the Royal College of Chemistry under the direction of Dr. Hofmann, to whom I beg to offer my best thanks for his advice and assistance during their progress.

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## XVIII.—*On the Action of Nitric Acid on Cymol.*

By H. M. Noad, Esq.

(Read before the Chemical Society of London, June 7, 1847).

### FORMATION OF TOLUYLIC AND NITROTOLUYLIC ACIDS.

We possess in benzoic acid and its derivatives a well-defined group of substances connected in a variety of ways with a large number of organic families. These interesting bodies have been made subjects of investigation by several chemists. The study has been a fascinating one, and has resulted in a thorough development of their history, and of the products of their decomposition.

This group may be considered the prototype, as it were, of several parallel groups, presenting a very close relation with the composition of the benzoyl family. The careful study of the former has gradually made these known to us, in the same manner as the study of alcohol and its derivatives made us acquainted with several corresponding classes of bodies.

The methyl compounds, with which we have become familiar through the experiments of Dumas and Peligot * on pyroxylic spirit,

* Liebig's Annalen, xv, 1.

and the amyl series, the origin of which we owe to the investigations of Cahours* on fusel oil, form two groups, the analogy of which with the alcohol series can be traced in every direction; they differ in composition from the former only by a multiple of $C_2 H_2$, thus:

$HO, C_2 H_3 O$ = hydrated oxide of methyl.
$HO, C_4 H_5 O$ = hydrated oxide of ethyl.
$HO, C_{10} H_{11} O$ = hydrated oxide of amyl.

The same relation is likewise observed in the acids resulting from the oxidation of these bodies, and these acids are perhaps even better adapted to point out this interesting regularity, as the gaps existing between the different alcohols are filled up in the series of the acids, which may be formed in a great variety of ways. A glance at the following table will render the regularity above alluded to at once obvious:

| Alcohols. | Acids. |
|---|---|
| $HO, C_2 H_3 O$, pyroxylic. | $H C_2 H O_4$, formic. |
| $HO, C_4 H_5 O$, vinic. | $H C_4 H_3 O_4$, acetic. |
| | $H C_6 H_5 O_4$, metacetonic. |
| | $H C_8 H_7 O_4$, butyric. |
| $HO, C_{10} H_{11} O$, amylic. | $H C_{10} H_9 O_4$, valerianic. |
| | $H C_{12} H_{11} O_4$, caproic. |
| | $H C_{14} H_{13} O_4$, œnanthylic. |
| | $H C_{16} H_{15} O_4$, caprylic. |
| | $H C_{18} H_{17} O_4$, pelargonic. |
| | $H C_{20} H_{19} O_4$, capric. |
| &c. | &c. |

Now it seems that benzoic acid is a member of a similar series of acids, distinguished from each other by the same amounts of carbon and hydrogen, and that we may expect to find a representative of every single term of the benzoyl series in these other families.

An examination of cumin oil by MM. Gerhardt and Cahours† has brought to light a new acid—cuminic acid,

$$H C_{20} H_{11} O,$$

which exhibits a perfect analogy with benzoic acid, not only in its physical properties, but also in the metamorphoses which it undergoes when acted on by chemical agents. This acid is distinguished from benzoic,

$$H C_{14} H_5 O,$$

* Liebig's Annalen, xxx, 288. † Ibid. xxxviii, 67.

by containing 3 ($C_2$ $H_2$) more; it stands to benzoic acid as valerianic acid stands to acetic acid, and when distilled with lime it is converted into cumol,

$$C_{18}\ H_{12},$$

which represents benzol,

$$C_{12}\ H_6,$$

in the benzoyle series. The same investigation of cumin oil has made us acquainted with another carbo-hydrogen cymol,

$$C_{20}\ H_{14},$$

which is also a representative of benzol in another series; but up to the present time the acid from which this carbo-hydrogen derives, and which would contain 4 ($C_2$ $H_2$) more than benzoic acid, has not been discovered.

By the investigations of Pelletier and Walter* on the products of the distillation of resinous substances; of Deville† on the distillation of tolu balsam, and of Boudault and Glenard‡ on the dry distillation of dragon's blood, an addition has been made to the number of carbo-hydrogens, and we have obtained knowledge of a new body, which was described by the first chemists under the name of retinaphtha, by the second under that of benzoène, and by the last under that of dracyl; for all three Berzelius§ has proposed the more appropriate name of toluol‖ ($C_{14}$ $H_8$); this body, which differs from benzol in containing $C_2$ $H_2$ more, also represents that carbo-hydrogen in a new family, a number of members of which has already become known. Thus Deville has shown, that on treating his toluol with sulphuric and nitric acids, the corresponding terms of hyposulphobenzolic acid, nitrobenzol, and dinitrobenzol are obtained.

* Liebig's Annalen, vol. xxviii, 295.

† Ann. de Chim. et Phys., 3 sér. t. iii, p. 168.

‡ Journ. de Pharm. et de Chim., 3 sér. t. vi, p. 250.

§ Jahresbericht, xxii, p. 354.

‖ On comparing the properties which Pelletier and Walter ascribe to retinaphtha with those of benzoène given by Deville, it is nearly certain that both substances are identical, though Deville seems to be inclined to establish a difference. A comparative study is, however, still wanting. Regarding dracyl, I may mention here that when engaged in the investigation of toluidine with Dr. Muspratt, we prepared a portion of this body according to the directions of Glenard and Boudault. The dracyl obtained possessed all the properties of toluol; we converted the body thus prepared into nitrodracyl (nitrotoluol), from which, by treatment with reducing agents, beautiful crystals of toluidine were obtained. In our paper on this organic base an analysis of the sulphate is given, and on referring I find that we forgot to mention that the salt analysed was prepared with the very toluidine obtained from the carbo-hydrogen arising among the distillation products of dragon's blood. This experiment removes any doubt that might have remained as to the identity of toluol and dracyl.—Dr. A. W. Hofmann.

Investigations on the action of nitric acid on oil of anise by Cahours,* and on Oleum dracunculi by Laurent,† have led to the discovery of anisylic, nitranisylic acids, and anisol (draconic, nitrodraconic acids and dracol), corresponding respectively to salicylic, nitrosalicylic acids and phenol; more recently Cahours‡ has found in hydride of anisyl even the term corresponding to hydride of salicyl, while Drs. Muspratt and Hofmann§ have produced the organic base corresponding to aniline; in the paper in which this new and remarkable substance is described, these gentlemen have given a table, in which the analogy between the anisyl and salicyl groups has been pointed out.

In order to render this parallelism complete, one principal term of the new series has hitherto been wanting, viz., the acid corresponding to benzoic acid. In the following paper will be pointed out the formation and properties of this substance, and the corresponding nitrogenous acid, both arising amongst the products of the oxidation of cymol.

## PREPARATION OF CYMOL.

The experiments of Gerhardt and Cahours have shown that cumin oil (*oleum cumini*) is a mixture of two distinct oils, — cuminol ($C_{20}$ $H_{12}$ $O_2$), a body corresponding closely to oil of bitter almonds, and cymol ($C_{20}$ $H_{14}$); by treatment with potassa, the oxygenated oil is converted into cuminic acid, while the carbo-hydrogen distils over unaltered. As for the experiments about to be detailed, it was the latter of these two oils that was required, the mode of separation which I found it most convenient to adopt was the following:—The oil was first submitted to distillation alone, and about two-thirds of it drawn over; this portion was then repeatedly distilled with sticks of caustic potassa, until the alkali remained unaltered; fresh potassa was introduced after every third or fourth distillation, and the oil was regarded as pure when it ceased to lose anything after two or three distillations; latterly I found it advantageous to employ a retort of copper in this operation, the heated alkali proving exceedingly destructive to vessels of glass. The quantity of cymol obtained averaged about 7 oz. for every pound of cumin oil; and here I must be allowed to express my thanks to my friend Mr. Warington for having kindly undertaken to furnish me with a supply of oil obtained directly from the seeds by distillation: without his assistance I should scarcely have been able to have followed out my investigation,

* Liebig's Annalen, XLI, 56.
† Ibid. XLIV, 313.
‡ Ibid. LVI, 307.
§ Mem. of Chem. Soc. vol. II, p. 367.

on account of the high price and varying quality of the oil obtained in commerce; from three-quarters of a hundred weight of seed Mr. Warington obtained in four distillations 2 lbs. 12 oz. of oil, which yielded me 18 oz. of perfectly pure cymol.

To render cymol perfectly anhydrous, it was left for some time in contact with pieces of fused chloride of calcium and again distilled; in this state it is a limpid, colourless, highly refracting oil, of a very agreeable odour; its specific gravity I found to be 0·8576 at $16^0$, and its boiling-point, as a mean of two determinations with two specimens of the oil obtained at different periods, and which agreed closely with each other, $171^0{\cdot}5$ C.

Cymol has been identified with camphogene, a substance previously obtained by Dumas,* by the action of anhydrous phosphoric acid on camphor, and lately studied by Delalande.† At the commencement of my experiments, I thought that this might probably be a useful practical method of procuring the carbo-hydrogen; from the difficulty, however, of obtaining anhydrous phosphoric acid in sufficient quantities, and from the small amount of camphogene obtained, I found it otherwise, and I merely prepared a sufficient supply to enable me to obtain an additional proof of the identity of the two oils, which I did in a manner hereafter to be described. I may remark, that even after repeated distillations with renewed quantities of anhydrous phosphoric acid, I was unable to procure camphogene quite free from the peculiar smell of camphor, nor was there to be discovered in it the slightest approach to that fragrant odour by which cymol is characterized.

### ACTION OF NITRIC ACID ON CYMOL.

The action of nitric acid on cymol or camphogene has never hitherto been the subject of minute examination. Gerhardt and Cahours in their paper only mention that nitric acid of moderate concentration does not attack cymol when cold; that on heating nitrous acid is disengaged, and the carbo-hydrogen gradually passes into a peculiar acid, which, on cooling, is precipitated as a curdy mass; that this acid is rather soluble in water, alcohol and ether, crystallizing only with difficulty, and decomposed by heat, partially subliming in fine light needles or woolly flakes; and that fuming nitric acid decomposes cymol with the formation of the same acid and a yellow resin; none of these substances were, however, submitted by these chemists to elementary analysis. Delalande states, that on

* Liebig's Annalen, vi, 249. † Ibid. xxxviii, 343.

treating camphogene with boiling fuming nitric acid, it is converted into a white solid matter, becoming crystalline in the acid, and containing nitrogen. From these statements it seemed evident that the action of nitric acid on cymol gives rise to a variety of bodies, a supposition which experiments have completely verified; indeed, by a careful examination of this reaction, I have ascertained that not less than five or six different substances are produced; these bodies, some of which are acid, and some of a neutral character, are separated, however, only with considerable difficulty. In the present Memoir, I propose to confine myself to the acids only, reserving the regular substitution products of cymol, with the basic bodies arising therefrom, the substances representing nitrobenzol, aniline, &c., in the cymol series for a future paper.

I commenced with fuming nitric acid of the highest degree of concentration, the action of which on cymol is exceedingly violent; to avoid explosions, it was necessary to keep the vessel cool by immersion in water; the oil was added gradually, drop by drop, to the acid, which speedily became of a dark red colour; by repeated distillations, I obtained a beautiful crystalline acid, the analysis of which, leading to the formula:

$$C_{16}\,H_7\,N\,O_8,$$

rendered it evident, from the mode of its formation, that it must be considered as a substitution product of a corresponding non-nitrogenous acid,

$$C_{16}\,H_8\,O_4,$$

the very acid that is wanting in the toluol series, to the production of which acid my attention was now particulary directed.

Many attempts were made to oxidize the oil without having recourse to nitric acid; long-continued distillations with chromic acid, or with binoxide of manganese and sulphuric acid proved quite ineffectual, but after a great number of tentative operations, I at length succeeded, by the following method, in obtaining the wished-for substance, for which I propose the name of *toluylic acid.* Ordinary nitric acid was diluted with about six times its bulk of water, and cymol added in the proportion of about 2 oz. of the oil to 1 lb. of the acid; the mixture was then introduced into a capacious retort, and the distillation continued for two or three days; with acid of this strength there is no fear of a violent action; the oxidation of the oil proceeds slowly and quietly; it first becomes of a bright blue colour, from the absorption of nitric oxide gas, then yellow, and after having been ten or a dozen times poured back into the retort, it

begins to change more and more its physical character; it becomes heavier and more tenacious, and finally sinks to the bottom of the vessel; the process is known to be completed by a portion of the newly-formed acid passing over with the vapour of water, and condensing in the receiver. If the whole operation has been successfully conducted, the contents of the retort become nearly solid on cooling from the crystallization of the acid; the weaker the nitric acid employed, and the longer the time consumed, the whiter and purer is the resulting product; if a much stronger acid than that above prescribed be employed, violent action takes place when the boiling-point is reached, nearly the whole of the contents of the retort is projected into the receiver, and the new acid is found at the close of the operation to be contaminated with a considerable quantity of the nitrogenous acid, from which it is impossible afterwards entirely to free it; even when the operation has been slowly and carefully conducted with a very weak acid, it still contains a certain quantity of the nitrogenous acid, as numerous analyses proved, from which it is only to be freed by a series of troublesome operations; and it was only after a careful study and comparison of the salts formed by the respective acids, that I was enabled to lay down a precise method for their separation. This method is founded on the great solubility of toluylate of barium in cold water, and the very sparing solubility of the corresponding salt of the nitrogenous acid in the same menstruum. The crude acid is thrown on a filter, and the adhering nitric acid removed by washing with cold water; it is then boiled with hydrate of lime, and the resulting lime-salt, filtered when quite cold, afterwards decomposed by nitric or hydrochloric acid; if the acid does not precipitate tolerably white, the same operation is repeated, and the well-washed acid is then dissolved in baryta water and carefully evaporated to dryness on the water-bath; it is redissolved in cold water, filtered, reprecipitated by hydrochloric acid, washed, and the process repeated until the dry barium salt dissolves completely in cold water; it should then be once or twice crystallized, after which it is generally quite pure.

The quantity of pure acid as thus obtained from 2 oz. of cymol is very small, but I have not hitherto been fortunate enough to discover a better or less circuitous method of procuring it; could an oxidizing action be effected on the oil without the use of nitric acid, a great saving would undoubtedly be achieved, but, as before stated, all my attempts in this direction proved unavailing; it is not impossible that the object may be obtained by permanganate of potassa. I made one experiment with this salt, and there was evidently a

reduction of the permanganic acid, but no trace of toluylic acid could be discovered, from which it seems evident that the oxidation had in this case proceeded too far, and the cymol become converted into carbonic acid; this reaction has not, however, as yet been sufficiently studied.

### COMPOSITION OF TOLUYLIC ACID.

On submitting toluylic acid to elementary analysis in the usual manner, by burning it with protoxide of copper, I obtained the following results:

I. Acid obtained by sublimation, not having been previously treated with baryta:
0·2225 grm. of acid gave:
0·5690 „ „ carbonic acid, and
0·1190 „ „ water.

II. Acid obtained as before from a new preparation:
0·2105 grm. of acid gave:
0·5400 „ „ carbonic acid, and
0·1130 „ „ water.

III. Acid obtained from the calcium salt:
0·1600 grm. of acid gave:
0·4150 „ „ carbonic acid, and
0·0850 „ „ water.

IV. Acid obtained from the barium salt:
0·3120 grm. of acid gave:
0·8030 „ „ carbonic acid, and
0·1610 „ „ water.

V. Acid obtained as before from a new preparation:
0·3200 grm. of acid gave:
0·8250 „ „ carbonic acid, and
0·1715 „ „ water.

These numbers correspond to the following per centages:

| | I. | II. | III. | IV. | V. |
|---|---|---|---|---|---|
| Carbon . . | 69·74 | 69·96 | 70·09 | 70·19 | 70·31 |
| Hydrogen . | 5.94 | 5·96 | 5·98 | 5·98 | 5·95 |

and with consideration of the atomic weight, as deduced from the analysis of the silver and barium salts, lead to the following formula:

$$C_{16} H_8 O_4,$$

as may be seen by the following comparison:

| | | Theory. | | Mean of the three last experiments. |
|---|---|---|---|---|
| 16 equiv. of Carbon . . . | 96 | 70·58 | 70·20 |
| 8 „ „ Hydrogen . . | 8 | 5·88 | 5·97 |
| 4 „ „ Oxygen . . . | 32 | 23·54 | — |
| 1 equiv. of Toluylic Acid . | 136 | 100·00 | |

This acid thus becomes isomeric with hydride of anisyle and benzoate of methyl.

### PROPERTIES OF TOLUYLIC ACID.

From an aqueous solution of any of its salts, toluylic acid is precipitated by nitric or hydrochloric acid as a snow-white curdy mass, which under the microscope resolves itself into a great number of small acicular crystals: it is soluble to a considerable extent in boiling water, out of which it crystallizes on cooling in small needles; in alcohol, ether and pyroxylic spirit, it is soluble almost to any extent; when heated, it fuses and sublimes without decomposition in beautiful needles; in its state of perfect purity, it is inodorous and tasteless; but the impure acid has a peculiar and sickening smell, somewhat resembling that of oil of bitter almonds. When boiled for some time, with concentrated nitric acid, it loses an atom of hydrogen, in the place of which an atom of hyponitric acid enters, nitrotoluylic acid being formed; and when heated with caustic lime or baryta, it is decomposed into carbonic acid and toluol.

In the formation of toluylic acid from cymol, four equivalents of carbon, and six equivalents of hydrogen are eliminated in the form of oxalic and carbonic acids and water. In several preparations large quantities of oxalic acid were found. There exists a striking similarity in the manner in which nitric acid acts upon cymol and oil of anise, an oil in its composition closely connected with cymol, and which gives rise to anisylic acid, between which and toluylic acid there is also a marked resemblance. The composition of oil of anise being

$$C_{20}\,H_{12}\,O_2,$$

we may consider it as cymol which has lost two equivalents of hydrogen and taken two of oxygen. The composition of the acids, formed by the action of nitric acid on these two oils, is as follows:

Toluylic acid . . . . . $C_{16}\,H_8\,O_4$,
Anisylic acid . . . . . $C_{16}\,H_8\,O_6$.

### COMPOUNDS OF TOLUYLIC ACID.

From the extreme difficulty of obtaining this acid in a state of purity in any quantity, I have not been able to examine as many of its salts as I could have wished; the following will, however, serve to confirm its composition and establish its atomic weight.

*Toluylate of barium.*—The formation of this salt has been already described; I was unable to obtain it in a well-defined crystalline form. Its analysis yielded the following result:

0·7955 grm. gave: 0·4530 sulphate of barium = 33·50 per cent. of barium, agreeing very closely with the formula,

$$Ba\ C_{16}\ H_7\ O_4,$$

as indicated by the subjoined comparison:

| | Theory. | | Experiment. |
|---|---|---|---|
| 1 equiv. of Barium . . . . | 68·64 | 33·70 | 33·50 |
| 1 „ „ Anhydride . . . | 135·00 | 66·30 | — |
| 1 eq. of Toluylate of Barium . | 203·64 | 100·00 | |

*Toluylate of silver.*—This salt was formed by dropping nitrate of silver into a perfectly neutral solution of toluylate of ammonium; it fell as a white curdy mass, which was washed on a filter with cold water, and purified by two or three crystallizations out of boiling water: it crystallizes in small needles. On analysing this salt the following numbers were obtained:

I. 0·3340 grm. of salt ignited gave:
0·1485 „ „ silver.
II. 0·1725 „ „ from another preparation gave:
0·0767 „ „ silver.
III. 0·1705 „ „ from a third preparation gave:
0·0757 „ „ silver.
IV. 0·3785 „ „ silver-salt, burned with protoxide of copper, gave:
0·5440 „ „ carbonic acid, and
0·1045 „ „ water.

These numbers correspond to the following per centages:

| | I. | II. | III. | IV. |
|---|---|---|---|---|
| Silver . . . | 44·46 | 44·46 | 44·40 | — |
| Carbon . . | — | — | — | 39·198 |
| Hydrogen . | — | — | — | 3·030 |

and lead to the formula,

$$Ag\ C_{16}\ H_7\ O_4,$$

as may be seen by the following comparison:

| | Theory. | | Experiment. |
|---|---|---|---|
| 1 equiv. of Silver . . . . . | 108 | 44·44 | 44·440 |
| 16 „ „ Carbon. . . . . | 96 | 39·51 | 39·198 |
| 7 „ „ Hydrogen . . . . | 7 | 2·88 | 3·030 |
| 4 „ „ Oxygen . . . . | 32 | 13·17 | — |
| 1 equiv. of Toluylate of Silver . | 243 | 100·00 | |

*Toluylate of copper.*—This salt was prepared by dropping a solution of sulphate of copper into a perfectly neutral solution of toluylate of potassium; it fell as a bright blue precipitate closely resembling the corresponding benzoate. It is very soluble in ammonia, forming a dark blue solution, and soluble to a slight extent in boiling water, separating on cooling as a granular precipitate; its analysis gave the following result:

0·3385 grm. ignited, the residue treated with nitric acid, and again ignited gave 0·0082 grm. of protoxide of copper = 19·20 per cent. of copper, agreeing with the formula:

$$Cu\ C_{16}\ H_7\ O_4.$$

| | Theory. | | Experiment. |
|---|---|---|---|
| 1 equiv. of Copper . . . . . | 31·70 | 19·01 | 19·20 |
| 1 „ „ Anhydride . . . . | 135·00 | 80·99 | — |
| 1 eq. of Toluylate of Copper . . | 166·70 | 100·00 | |

*Toluylate of ethyl.*—This compound was formed by transmitting a stream of dry hydrochloric acid gas through a solution of the acid dissolved in strong alcohol, until the latter fumed strongly; it was then distilled, about two-thirds drawn over, and the residue in the retort mixed with water; the new ether precipitated in the form of a dark heavy liquid; it was digested with ammonia to remove any uncombined toluylic acid, well washed with distilled water, dried, by being allowed to remain for some time in contact with pieces of fused chloride of calcium, and then distilled: it passed into the receiver nearly colourless, but on standing it deposited a small quantity of crystalline matter, which proved to be the ether of the nitrogenous acid, the acid employed not having been obtained from the barium salt. By a second distillation, collecting only the first portions, the whole of the other ether was removed, and a pure substance obtained.

0·2230 grm. of ether gave:
0·5960 „ „ carbonic acid, and
0·1510 „ „ water.

Centesimally:

| | |
|---|---|
| Carbon . . . . . | 72·90 |
| Hydrogen . . . . | 7·52 |

agreeing closely with the formula:

$$C_4 H_5, C_{16} H_7 O_4,$$

as the following comparison of the theoretical with the experimental numbers shows:

| | Theory. | | Experiment. |
|---|---|---|---|
| 20 equiv. of Carbon . . . | 120 | 73·17 | 72·90 |
| 12 „ „ Hydrogen . . . | 12 | 7·31 | 7·52 |
| 4 „ „ Oxygen . . . | 32 | 19·52 | — |
| 1 eq. of Toluylate of Ethyl . | 164 | 100·00 | |

When perfectly pure, this compound is a colourless, fragrant liquid, having an odour closely resembling that of cinnamic or benzoic ether, and a pungent and slightly bitter taste. It boils at 228° C., which temperature may, perhaps, be one or two degrees too high, the determination having been made before the last traces of the nitrogenous ether had been removed; still it exhibits a new confirmation of the observation of H. Kopp, that the difference in the boiling-points of two analogous compounds, which differ by two equivalents of carbon and two of hydrogen, is 19° C. Benzoic ether, the composition of which is

$$C_4 H_5, C_{14} H_5 O_4,$$

boils at 209°. Unfortunately I had not a sufficient quantity of the liquid after purification for a second determination.

The following salts I have examined qualitatively only, considering the composition and atomic weight of the acid sufficiently well established by the preceding analyses.

*Toluylate of potassium*, formed by exactly neutralizing the acid with caustic potassa, is a very soluble salt, crystallizing with great difficulty in small needles.

*Toluylate of sodium* is still more soluble than the preceding. I could not obtain it in the crystalline state.

*Toluylate of ammonium* crystallizes in small prisms.

*Toluylate of calcium* crystallizes out of a concentrated aqueous solution in long shining needles.

### PRODUCTS OF THE DECOMPOSITION OF TOLUYLIC ACID.

*Nitrotoluylic acid.*—I have already observed, that on treating cymol with concentrated and fuming nitric acid, violent action ensues, and that by repeated distillations a crystalline acid, containing nitrogen, is obtained. I must now describe this action more in detail. The nitric acid employed should be concentrated and fuming, otherwise there will be a considerable formation of another crystalline substance, which is in its chemical character neutral, and which is not easily converted into nitrotoluylic acid. The properties and composition of this new product will be fully considered hereafter. The distillation must be continued as long as nitrous fumes continue to be evolved, and the retort then allowed to cool, upon which a considerable quantity of crystalline matter is deposited, and on adding cold water, a copious precipitate takes place. The whole is now thrown on a filter, and washed with cold water till all the nitric acid is removed; the precipitate is then digested with ammonia, the greater part dissolves; a portion, however, collects at the bottom of the vessel in the form of a red oil, which is to be separated. The ammonium salt is next decomposed by hydrochloric acid, the acid collected on a filter and well washed with cold water, in which it is very sparingly soluble; it is then dissolved in hot alcohol, boiled for a few minutes with animal charcoal, and filtered; by spontaneous evaporation, the new acid crystallizes out in beautiful rhombic prisms of a pale yellow colour.

### COMPOSITION OF NITROTOLUYLIC ACID.

The powdered crystals by combustion with protoxide of copper yielded the following numbers:

| | | | |
|---|---|---|---|
| I. | 0·3300 | grm. | of acid gave: |
| | 0·6400 | „ | „ carbonic acid, and |
| | 0·1205 | „ | „ water. |
| II. | 0·3820 | „ | „ acid gave: |
| | 0·7396 | „ | „ carbonic acid, and |
| | 0·1360 | „ | „ water. |
| III. | 0·4145 | „ | „ acid gave: |
| | 0·8060 | „ | „ carbonic acid, and |
| | 0·1520 | „ | „ water. |

IV. The nitrogen was determined by Dumas' method in an atmosphere of carbonic acid. The particulars of the experiment are as follows:

0·600 grm. of acid gave: 41·5 cubic cent. of moist nitrogen. Barometer 0m·7973; Thermometer 18°·5 C.

These numerical results correspond with the following per centage composition:

| | I. | II. | III. | IV. |
|---|---|---|---|---|
| Carbon . . | 52·89 | 52·80 | 53·03 | — |
| Hydrogen . | 4·06 | 3·95 | 4·07 | — |
| Nitrogen . . | — | — | — | 79·6 |

and lead to the formula,

$$C_{16}\left\{\begin{matrix}H_7\\NO_4\end{matrix}\right\}O_4,$$

as the following comparison of the calculated numbers with the mean of analysis shows:

| | Theory. | | Mean of experiment. |
|---|---|---|---|
| 16 equiv. of Carbon . . . . | 96 | 53·03 | 52·90 |
| 7 „ „ Hydrogen . . . | 7 | 3·86 | 4·00 |
| 1 „ „ Nitrogen . . . | 14 | 7·74 | 7·96 |
| 8 „ „ Oxygen . . . | 64 | 35·37 | — |
| 1 equiv. of Nitrotoluylic Acid | 181 | 100·00 | |

By the following analyses of some of the salts of this acid, the above formula is fully confirmed, and the atomic weight of the acid proved.

*Nitrotoluylate of barium.*—This salt was formed by adding chloride of barium to a neutral solution of nitrotoluylate of ammonium. A white curdy precipitate was determined, soluble to a considerable extent in boiling water, out of which it crystallized on cooling in beautiful stellated tufts, having a shining appearance when dry; after two or three recrystallizations, it was submitted to analysis, and yielded the following results:

0·7380 grm. of the salt gave, by ignition, 0·2900 grm. of carbonate of baryta = 27·23 per cent. of barium, corresponding with the formula:

$$Ba\ C_{16}\left\{\begin{matrix}H_6\\NO_4\end{matrix}\right\}O_4,$$

as may be seen by the following comparison:

| | Theory. | | Experiment. |
|---|---|---|---|
| 1 equiv. of Barium . . . . . | 68·70 | 27·68 | 27·23 |
| 1 „ „ Anhydride . . . . . | 179·50 | 72·32 | — |
| 1 equiv. of Nitrotoluylate of Barium . | 248·20 | 100·00 | |

*Nitrotoluylate of silver.* — This salt was formed by dropping nitrate of silver into a neutral solution of nitrotoluylate of ammonium; it fell as a white curdy mass resembling chloride of silver. It is soluble to a considerable extent in hot water, and by long boiling becomes partially decomposed; it crystallizes from a hot aqueous solution in beautiful feathery tufts; it is only sparingly soluble in alcohol.

By analysis, the following results were obtained:

I. 0·3385 grm. of silver-salt gave:
0·1270 „ „ silver.
II. 0·2300 „ „ silver-salt gave:
0·0860 „ „ silver.
III. 0·3505 „ „ silver-salt gave:
0·4240 „ „ carbonic acid, and
0·0700 „ „ water.

Centesimally:

| | I. | II. | III. |
|---|---|---|---|
| Silver . . | 37·52 | 37·38 | — |
| Carbon . | — | — | 33·00 |
| Hydrogen | — | — | 2·12 |

corresponding with the formula:

$$Ag\,C_{16}\left\{\begin{matrix}H_6\\NO_4\end{matrix}\right\}O_4.$$

| | Theory. | | Experiment. |
|---|---|---|---|
| 1 equiv. of Silver . . . . . | 108 | 37·51 | 37·45 |
| 16 „ „ Carbon . . . . . | 96 | 33·33 | 33·00 |
| 6 „ „ Hydrogen . . . . . | 6 | 20·80 | 2·12 |
| 1 „ „ Nitrogen . . . . . | 14 | 4·86 | — |
| 8 „ „ Oxygen . . . . . | 64 | 22·22 | — |
| 1 equiv. of Nitrotoluylate of silver | 288 | 100·00 | |

I have already mentioned that I prepared a small quantity of camphogene by the action of anhydrous phosphoric acid on camphor; in order to obtain an additional experimental proof of the identity of this substance with cymol, I have studied the action of concentrated nitric acid on it. I found it most convenient to prepare a silver-salt of the acid thus obtained, the analysis of which yielded me the following numbers:

I. 0·3720 grm. of silver-salt gave:
0·1390 „ „ silver.
II. 0·2935 „ „ silver-salt gave:
0·1100 „ „ silver.
III. 0·3960 „ „ silver-salt gave:
0·4860 „ „ carbonic acid, and
0·8500 „ „ water.

These numbers correspond to the per centage composition:

| | I. | II. | III. |
|---|---|---|---|
| Silver . . . . | 37·36 | 37·47 | — |
| Carbon . . . . | — | — | 33·46 |
| Hydrogen . . . | — | — | 2·38 |

By comparing those numbers with the preceding, they will be found sufficiently near to warrant the conclusion that the two carbo-hydrogens are identical. On treating the acid formed by the action of fuming nitric acid on camphogene with ammonia, the same heavy oil which was observed in the case of cymol separated, and after a while crystallized; but from the small quantity of camphogene at my command, I was unable to procure sufficient of this substance for a comparative experiment, or to bring forward any additional proof of the identity of the two oils.

*Nitrotoluylate of calcium.*—This salt was prepared by decomposing nitrotoluylate of ammonium by chloride of calcium. It fell as a granular crystalline mass, much more soluble in water than the corresponding barium salt, and crystallizing out of its aqueous solution in small clustering groups of oblique rhombic prisms; it was obtained perfectly pure by two or three recrystallizations.

0·6965 grm. of calcium salt gave by ignition, treatment with carbonate of ammonia, and a second gentle ignition, 0·1775 grm. of carbonate of lime = 10·19 per cent. of calcium, agreeing exactly with the formula:

$$Ca\,C_{16}\left\{\begin{matrix}H_6\\NO_4\end{matrix}\right\}O_4.$$

| | Theory. | | Experiment. |
|---|---|---|---|
| 1 equiv. of Calcium . . . . . | 20·00 | 10·02 | 10·19 |
| 1 „ „ Anhydride . . . . . | 179·50 | 89·98 | — |
| 1 eq. of Nitrotoluylate of Calcium | 199·50 | 100·00 | |

*Nitrotoluylate of ethyl.*—A solution of the pure acid, in strong alcohol, was submitted to a current of dry hydrochloric acid gas till copious fumes were evolved; it was then distilled; the first portions that passed into the receiver consisted of a mixture of alcohol and hydrochloric ether; the distillation was continued until a few drops collected on a watch-glass gave a milkiness when mixed with water; it was then stopped, and the retort allowed to cool; a considerable quantity of the yellow heavy oil collected at the bottom of the vessel, which was poured off into a beaker; in a few minutes it solidified into a yellow crystalline mass. This impure ether was next treated with carbonate of potassa, by which all adhering undecomposed acid was removed; it was then thrown on a filter, well washed with cold water, and dried by pressure between folds of bibulous paper; it was now of a pale amber colour, and possessed a very agreeable odour; redissolved in hot alcohol and filtered, the alcoholic solution on cooling solidified into a light lemon-coloured crystalline mass; this was dried between folds of blotting-paper, transferred to a watch-glass, and, placed in the water-bath, when it immediately liquefied: after remaining about an hour, it was removed, and on cooling it gradually crystallized into a mass of needles radiating from a common centre, and having a very beautiful appearance.

It was analysed by combustion with protoxide of copper, and furnished the following results:

0·3620 grm. of ether gave:
0·7600 „ „ carbonic acid, and
0·1750 „ „ water.

Centesimally:

| | |
|---|---|
| Carbon . . . . . | 57·26 |
| Hydrogen . . . . . | 5·37 |

agreeing with the formula:

$$C_4\,H_5,\,C_{16}\left\{\begin{matrix}H_6\\NO_4\end{matrix}\right\}O_4,$$

as shown by the following comparison:

| | Theory. | | Experiment. |
|---|---|---|---|
| 20 equiv. of Carbon . . . . . | 120 | 57·42 | 57·26 |
| 11 „ „ Hydrogen . . . . . | 11 | 5·26 | 5·37 |
| 1 „ „ Nitrogen . . . . . | 14 | 6·69 | — |
| 8 „ „ Oxygen . . . . . | 64 | 30·63 | — |
| 1 equiv. of Nitrotoluylate of Ethyl | 209 | 100·00 | |

The remainder of the ether was dissolved in a strong alcoholic solution of ammonia, and set aside with the view of procuring nitrotoluylamide: this substance, however, which it would have been interesting to have compared with the corresponding term of the benzoyl series, lately obtained by Mr. Field,* I have not yet been able to obtain.

*Nitrotoluylate of methyl.*—To prepare this substance, nitrotoluylic acid was dissolved in pure pyroxylic spirit, and the solution subjected to a long-continued stream of dry hydrochloric acid gas, as in the corresponding ethyl compound. On distilling the fuming acid liquid, a considerable quantity of a dense, black oily substance collected at the bottom of the vessel: this was evidently the methyl compound contaminated with products of the decomposition of the pyroxylic spirit by the hydrochloric acid gas. On cooling the acid liquid was poured off, and the oil repeatedly washed with water, in a few hours it solidified into a confused crystalline mass, still however black, and having a peculiar vinous smell: an attempt was made to purify it by distillation with water; in consequence, however, of its high boiling-point, very little passed over into the receiver after two or three hours' heating. It was then mixed with strong nitric acid, and after boiling for a few minutes water was added; the ether now readily separated in clear, light yellow oily drops: ammonia was then added to remove any nitrotoluylic acid that might have been present, and the oil collected on a watch-glass; in a few minutes it solidified into a crystalline mass, which was dissolved in ether, filtered and recrystallized, and then exposed for some time to the heat of the water-bath; on cooling it solidified as before, and was then considered sufficiently pure for analysis.

0·3760 grm. of ether gave by combustion with protoxide of copper:
0·7560 „ „ carbonic acid, and
0·1640 „ „ water, corresponding to the following per centage.

| | |
|---|---|
| Carbon . . . . . | 54·84 |
| Hydrogen . . . . . | 4·83 |

and agreeing with the formula:

$$C_2 H_3, C_{16} \left\{ \begin{matrix} H_6 \\ NO_4 \end{matrix} \right\} O_4.$$

* Researches of the Royal College of Chemistry, vol. i, p. 195.

| | Theory. | | Experiment. |
|---|---|---|---|
| 18 equiv. of Carbon . . . . . | 108 | 55·38 | 54·84 |
| 9 „ „ Hydrogen . . . . . | 9 | 4·61 | 4·83 |
| 1 „ „ Nitrogen . . . . . | 14 | 7·18 | — |
| 8 „ „ Oxygen . . . . . | 64 | 32·83 | — |
| 1 Nitrotoluylate of Methyl . . . | 195 | 100·00 | |

After standing two or three days, beautiful colourless stellar crystals were deposited on the sides of the vessel containing an aqueous solution of this ether; it is probable, therefore, that this as well as the last-described compound is, when perfectly pure, colourless. The two ethers closely resemble each other in their physical characters, the smell of the latter is, however, less agreeable than that of the former; both are decomposed by potassa into nitrotoluylic acid and alcohol or pyroxylic spirit.

The following salts of this acid I merely examined qualitatively.

*Nitrotoluylate of potassium* is a very soluble salt, crystallizing with great difficulty in small needles.

*Nitrotoluylate of sodium*, like the corresponding salt of toluylic acid, I could not obtain in any definite crystalline form.

*Nitrotoluylate of ammonium* crystallizes out of its aqueous solution in long needles; it is very easily decomposed, losing the whole of its ammonia when boiled with animal charcoal. I intend to return to the study of this salt, and hope to obtain from it the body which I failed to procure from nitrotoluylic ether, viz.: nitrotoluylamide.

*Nitrotoluylate of strontium.*—This salt, which in appearance is not to be distinguished from the corresponding barium salt, was formed by dropping chloride of strontium into neutral nitrotoluylate of ammonium: it is rather more soluble in boiling water than the barium compound, and the crystals deposited on cooling are rather larger.

*Nitrotoluylate of copper.*—On adding solution of sulphate of copper to perfectly neutral nitrotoluylate of ammonium, a basic salt is formed. I have not yet obtained a definite copper-salt of this acid.

The following table exhibits the compounds of toluylic and nitrotoluylic acids analysed:

| | |
|---|---|
| Toluylic acid . . . . . | $H\ C_{16}\ H_7\ O_4$ |
| Toluylate of barium . . . . | $Ba\ C_{16}\ H_7\ O_4$ |
| Toluylate of silver . . . . | $Ag\ C_{16}\ H_7\ O_4$ |
| Toluylate of copper . . . . | $Cu\ C_{16}\ H_7\ O_4$ |
| Toluylate of ethyl . . . . . | $C_4H_5\ C_{16}\ H_7\ O_4$ |
| Nitrotoluylic acid . . . . . | $H\ C_{16}\left\{\begin{matrix}H_6\\NO_4\end{matrix}\right\}O_4$ |
| Nitrotoluylate of barium . . | $Ba\ C_{16}\left\{\begin{matrix}H_6\\NO_4\end{matrix}\right\}O_4$ |
| Nitrotoluylate of calcium . . | $Ca\ C_{16}\left\{\begin{matrix}H_6\\NO_4\end{matrix}\right\}O_4$ |
| Nitrotoluylate of silver . . . | $Ag\ C_{16}\left\{\begin{matrix}H_6\\NO_4\end{matrix}\right\}O_4$ |
| Nitrotoluylate of ethyl . . . | $C_4H_5\ C_{16}\left\{\begin{matrix}H_6\\NO_4\end{matrix}\right\}O_4$ |
| Nitrotoluylate of methyl . . | $C_2H_3\ C_{16}\left\{\begin{matrix}H_6\\NO_4\end{matrix}\right\}O_4$ |

### ACTION OF A MIXTURE OF SULPHURIC AND NITRIC ACIDS ON NITROTOLUYLIC ACID.

When nitrobenzol is boiled repeatedly with the strongest nitric acid it loses an atom of hydrogen, in the place of which another atom of hyponitric acid enters. The transformation proceeds very slowly. The new substance (dinitrobenzol), is however, obtained very speedily, as Drs. Muspratt and Hofmann* have shown, by dropping benzol or nitrobenzol into a mixture composed of equal parts of fuming nitric acid and concentrated sulphuric acid as long as the liquid remains homogeneous. This method has lately been employed with great success by M. Cahours, who, amongst many other interesting products, has obtained:

Dinitrocuminic acid . . . $C_{20}\left\{\begin{matrix}H_{10}\\2(NO_4)\end{matrix}\right\}O_4$; and

Dinitrobenzoic acid . . . $C_{14}\left\{\begin{matrix}H_4\\2NO_4\end{matrix}\right\}O_4$.

It appeared interesting to submit nitrotoluylic acid to a similar treatment, but after digesting the acid with the mixture for several days, the anticipated transformation had not taken place, the numbers obtained by analysis being those given under III., "composition of nitrotoluylic acid." I intend, however, to repeat this experiment.

* Mem. Chem. Soc. vol. III, p. 111.

DISTILLATION OF TOLUYLIC ACID WITH BARYTA—TOLUOL.

Although the preceding analyses of toluylic and nitrotoluylic acids had established the composition of these two compounds in a perfectly satisfactory manner, there still remained one experiment to be made in order to prove that toluylic acid occupies in the toluyl series the same place which benzoic acid has in the benzoyl series; in order to prove that the acids analysed are really the true toluylic and nitrotoluylic acids, and not merely bodies having the same composition, being isomeric with them: this experiment was to attempt the transformation of toluylic acid into toluol under the same circumstances by which benzoic acid becomes converted into benzol. I devoted the acid from four ounces of cymol to this experiment, and by distillation with caustic baryta, which I found to answer much better than lime, I obtained several grammes of a beautiful limpid colourless liquid, having the precise smell of the carbo-hydrogen sought for. By distillation from a fresh portion of baryta, the oil was rendered perfectly anhydrous; in this state its boiling-point was taken. It began to boil at 109°, the thermometer gradually rose to 110°·5, barometer 0m·763 (30·1 inches).

It was burned in the ordinary manner with protoxide of copper, and yielded the following results:

0·2410 grm. of oil gave:
0·8090 „ „ carbonic acid, and
0·1960 „ „ water,

corresponding to the following per centage composition:

| | |
|---|---|
| Carbon . . . . . | 91·50 |
| Hydrogen . . . . . | 9·03 |

and agreeing exactly with the formula of toluol:

$$C_{14}\,H_8,$$

as the following comparison shows:

| | | Theory. | | Experiment. |
|---|---|---|---|---|
| 14 equiv. of Carbon . . . . | 84 | 91·3 | | 91·50 |
| 8 „ „ Hydrogen . . . | 8 | 8·7 | | 9·03 |
| 1 equiv. of Toluol . . . . . | 92 | 100·0 | | 100·53 |

The formation of toluol from toluylic acid is perfectly analogous to the production of benzol from benzoic acid.

$$\underbrace{C_{16}H_8O_4}_{\text{Toluylic acid.}} + 2BaO = \underbrace{C_{14}H_8}_{\text{Toluol.}} + 2(BaO, CO_2).$$

The remainder of the carbo-hydrogen was converted into nitrotoluol by the action of fuming nitric acid: the well-washed oily fluid was then dissolved in alcohol, saturated with ammoniacal gas, and treated repeatedly with sulphuretted hydrogen, the whole being distilled after each saturation with hydrosulphuric acid, to facilitate the deposition of the sulphur; the dark red solution was evaporated to expel the alcohol, water added, and then submitted to distillation with potassa; in addition to ammonia and aqueous vapour, a yellow oil passed into the receiver, which did not however solidify on cooling, probably in consequence of the presence of ammonia; it was therefore saturated with oxalic acid, evaporated to dryness in the water-bath, redissolved in boiling alcohol and filtered; on cooling, oxalate of toluidine separated in fine white needles, these were washed, dissolved in boiling water, and decomposed by potassa; the toluidine, which separated in colourless oily drops, was taken up by ether, on the evaporation of which it remained in the form of a crystalline mass. Although the nature of this substance was sufficiently obvious, nevertheless, to remove all doubt respecting it, I converted it into the double platinum-salt by mixing it with hydrochloric acid and bichloride of platinum. The beautiful orange-yellow spangular mass was washed with ether and dried in the water-bath. Its analysis gave the following result:

0·9300 grm. of the platinum-salt gave by ignition 0·2920 grm. of platinum = 31·39 per cent.

This determination agrees with the formula of the toluidine-platinum salt:

$$C_{14}H_9N, HCl, PtCl_2.$$

| | Theory. | | Experiment. |
|---|---|---|---|
| 14 equiv. of Carbon . . . . . | 84·00 | 26·91 | — |
| 9 „ „ Hydrogen . . . . . | 9·00 | 2·88 | — |
| 1 „ „ Nitrogen . . . . . | 14·00 | 4·49 | — |
| 3 „ „ Chlorine . . . . . | 106·50 | 34·11 | — |
| 3 „ „ Platinum . . . . . | 98·68 | 31·61 | 31·39 |
| 1 equiv. of Platinum-salt . . . | 312·18 | 100·00 | |

By the production of toluylic and nitrotoluylic acids, there is not only filled up a gap which has hitherto existed in the toluyl series,

but an important step has been made in the series of acids to which I have alluded at the commencement of this paper, of which, indeed, at the present time, a few scattered members only are known. The annexed table presents a general view of some of the most important members of the different groups, and exhibits the gaps which remain to be filled up by future experiments.

The table shows that there are, indeed, a great number of substances still to be discovered. In the first series, it will be seen that as yet we have only one member, semi-napthalidine, the base corresponding to aniline and toluidine, and obtained by Zinin in a very curious reaction of sulphide of ammonium on dinitronaphthalol. The second series is best known; it is closely connected with the indigo series by salicylic acid, nitrosalicylic acid and aniline. As, however, the term of indigo is as yet not represented in any of the other families, I have omitted to connect them. The third is the toluyl series, which has become enriched by the present investigation with two of the principal terms: of the following, no term whatever is known. The next contains a series of interesting compounds arising from oil of cumin, and of the last group we have at present only cymol. In a future Paper, I hope to introduce some of the substances deriving from this carbo-hydrogen.

This investigation was conducted in the laboratory of the Royal College of Chemistry, and I cannot bring it to a conclusion without acknowledging the great obligation I am under to Professor Hofmann for the constant advice and assistance which he afforded me during its prosecution, and expressing my warmest thanks to him for his valuable instructions in the method of conducting organic investigations generally.

| I. | V. | VI. |
|---|---|---|
| H $C_{..}$ $O_6$ unknown. | H $C_{20}$ $H_{11}$ $O_6$ unknown. | H $C_{22}$ H… unknow… |
| .. .. | | |
| .. .. | | |
| .. .. | Hydride of cuminyl H $C_{20}$ $H_{10}$ $O_2$ | .. .. |
| .. .. | Cuminic acid . . H $C_{20}$ $H_{11}$ $O_4$ | .. .. |
| .. .. | Nitrocuminic acid . H $C_{20}$ $\{H_{10} NO_4\}$ $O_4$ | .. .. |
| .. .. | Dinitrocuminic acid H $C_{20}$ $\{H_9 2NO_4\}$ $O_4$ | .. .. |
| .. .. | Cumonitrile . . $C_{20}$ $H_{11}$ N | . . |
| .. .. | Cumol . . . . $C_{18}$ $H_{12}$ | Cymol, $C_{2}$… |
| .. .. | Nitrocumol . . $C_{18}$ $\{H_{11} NO_4\}$ | .. .. |
| .. .. | Dinitrocumol . . $C_{18}$ $\{H_{10} 2NO_4\}$ | .. .. |
| Seminaphthalidine | Cumidine . . . $C_{18}$ $H_{13}$ N* | .. .. |
| .. .. | .. .. .. .. .. .. | .. .. |
| .. .. | .. .. .. .. .. .. | .. .. |
| .. .. | .. .. .. .. .. .. | .. .. |
| .. .. | .. .. .. .. .. .. | .. .. |

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# XIX.—*Researches on Coal Tar.*

By Charles Blachford Mansfield, B.A.

(Read before the Chemical Society of London.)

## Part I.

*Introductory remarks.*—The products of the destructive distillation of matters of complex and indeterminate composition are deficient in the interest which attaches to products, the constitutional relations of which to the bodies from whose decomposition they result, may be traced in the phenomena attending the process, or in the nature of the original substances. The absence of retrospective interest is, however, compensated to some extent in the case of pyrogenous products, which are obtained in large quantities from established processes in the arts; firstly, when they are viewed as primitive materials demanding, with the rest of nature, to be interpreted and applied by human industry (for the artificial is only a particular case of, and nowise distinct from, the natural); and, secondly, by the prospective interest connected with the distinct substances of much scientific importance, which may be isolated from them in abundance, but which can be obtained only in minute quantities from the other sources which are known to afford them. It is remarkable, however, that modern chemistry, with its rapid strides, has left on this extensive field but few foot-prints, whose impressions are distinct and likely to be durable. Although numerous researches, connected with very eminent names, show that the importance of a correct natural history of the substances known as tars, has not escaped the consideration of chemists, yet the meagre and indefinite details on these subjects, which are to be found in our scientific manuals, indicate that much yet remains to be accomplished.

The acid and basic components of the tars (and some of the ingredients of the aqueous parts of the products of distillation), have been more fortunate than their neutral associates in having been submitted to investigation, and designated by names, but there can be little doubt that, even of these, there are others awaiting the friendly hand of the chemist to redeem them from obscurity. Our acquaintance with the constitution of the neutral oils of the various tars has been, with few exceptions, limited to the fact that they are mixtures of various hydrocarbons, of which but few are announced as

having been separated, and, of these few, a still smaller fraction can claim satisfactory evidence of having been successfully isolated.

The examination of the fluid resulting from the compression of oil-gas * by Faraday, and that of resin tar by Pelletier and Walter,† are almost the only researches upon the neutral liquid pyrogenous oils, which have yielded exact results; and, in the latter of these instances, the partial nature of the methods employed render it probable that the subject was far from exhausted, since, for instance, the wholesale and assiduous treatment with concentrated sulphuric acid, to which the products were subjected, would probably exclude from the final results some substances of a neutral nature, which were unable to resist the action of that agent.‡ It is evident, from the unsatisfactory accounts which we receive of the eupion, obtained by Reichenbach from wood tar and from animal tar, that hydrocarbons have been confounded under this one name, which possess properties very different one from another, so that the whole subject, so far as relates to their neutral oils, requires re-examination. The oils of coal tar have been in the same predicament; it appears somewhat strange that, in this country, where coal tar is so exceedingly plentiful, our chemists should have been contented with the discovery of naphthaline, and should have allowed others, less fortunate than ourselves in being able to command abundance of this almost national production, to inform us of the existence at our feet of vast quantities of aniline, of paranaphthaline, and of other remarkable substances; and it appears, perhaps, no less singular that we should have failed as yet in applying them, when discovered, to the practical uses, which they will, no doubt, some day claim.

These considerations would render it unnecessary that Dr. Hofmann should back with much persuasion his suggestions to a student to undertake the further examination of coal tar. The researches, a portion of which it is the object of the present Paper to communicate, were commenced at the request of Dr. Hofmann, and were conducted, thus far, chiefly in the laboratory of the College of Chemistry, under his valued and friendly advice. It has been, perhaps, the tedium of the methods necessary to effect a separation of mixed hydrocarbons from each other, which has deterred experienced chemists from devoting their time to disentangling the oils here treated of: and, perhaps, to have conducted the innumerable dis-

* Transactions of the Royal Society, 1825.

† Annales de Chimie et de Physique, 1838. t. LXVII, p. 269.

‡ Vide not., p. 237.

tillations necessary for this purpose in a laboratory imperfectly furnished with gas and other conveniences, would have been a task too laborious to have been persisted in.

It may confer an interest upon the subject of this paper, if what has been hitherto known of the constitution of coal tar, be briefly epitomized; for the details which we possess on this subject are scattered few and far between over the various journals of European science, and the digests of this information to be found in our manuals, are by no means complete or accurate.

*Of coal tar as hitherto described.*—The term coal tar is here, as usually, applied to the black oily matter produced in the distillation of the varieties of bituminous coal, at high red heats, for the production of illuminating gas, as is ordinarily practised in gas-works. The substances which may be obtained by distilling the coal at lower temperatures are not here considered: indeed, but little is known at present of the modifications produced in the distillates, by variations of temperature in the retorts, or of the general relation between the character of the products, and the nature of the coal decomposed.

This coal tar, then, is known to be made up of numerous oily constituents, neutral, acid and basic; the neutral members of which assemblage form an overwhelming majority, and have not yet commanded the attention they deserve. It is remarkable, however, that of each of these classes, one representative has taken a leading position in the development of some of the most interesting facts of modern chemistry; than naphthaline, aniline, and phenole, few substances have contributed more by their products of substitution, and by the relations which they exhibit with other bodies, to the extension of the theory of compound radicals.

Among the acids of coal tar may be mentioned acetic acid, some of the acids of the cyanic series, and hydrosulphuric acid; but these belong rather to the aqueous liquor, than to the oily part, of the distillate. Of the acid oils we know but little. Runge* described three, which he denominated carbolic, rosolic, and brunolic acids. Of rosolic, and brunolic acids we have heard no more since Runge spoke of them, and their existence must be considered doubtful. The presence, however, of carbolic acid in the tar has been confirmed by Laurent,† who has analysed and described it under the name of hydrated oxide of phenyle (phenole, $C_{12}$ $H_5$ O, HO). It is probable

* Poggendorf's Annalen, Bd. 31, s. 65, 513, and Bd. 32, s. 308, 328.

† Annales de Chimie et de Physique, Sér. 3, t. III, p. 196.

also that, unless the creosote, which Reichenbach* prepared from wood tar, be the same substance in an impure state, that creosote also is present.

Of basic substances, ammonia abounds, and Runge† introduced three others into notice: pyrrol, kyanol (aniline $C_{12}$ $H_7$ N) and leucol (leukoline, $C_{18}$ $H_8$ N), the two last of which Dr. Hofmann‡ has placed, by his analyses, on the list of chemical realities. Of pyrrol nothing is known except that, according to Runge's account of it, it is a gaseous substance, that exists in very minute quantities in the oil of coal tar, as well as in animal tar. From Runge's description, the basic quality, which he assigns to it, seems rather doubtful; however, it is certain that the crude oil, especially the more volatile portion of it, does give the red colour to pine-wood dipped in hydrochloric acid, which Runge mentions as characteristic of pyrrol, and that it loses this property after agitation with a sufficient quantity of dilute acid. More recently, Dr. Anderson,§ of Edinburgh, has isolated and analysed the remarkable base, picoline, ($C_{12}$ $H_7$ N, isomeric with aniline), whose peculiar odour prevails in the more volatile coal-oils.

Of neutral substances, the solid hydrocarbon naphthaline ($C_{20}$ $H_8$) is universally known, and is remarkable as existing in such enormous quantities in some samples of tar, as to form nearly a quarter of the whole mass; while in others there is so little of it, that to obtain it at all is a matter of some difficulty.‖ Paranapthaline ($C_{30}$ $H_{12}$ ?) another beautiful solid, vastly abundant too, is less known, having

* Schweigger Seidel's Journal, Bd. 65, s. 461.

† Pogg. Annal. loc. sup. cit.

‡ Annalen der Pharmacie, Bd. 47, s. 37, and Philosophical Magazine, 1844, March and April.

§ Edinburgh New Philosophical Journal, 1846, July.

‖ There probably was but little naphthaline in the tars from which it was originally obtained, for Kidd, who first described a method of preparing it from coal tar (Philosophical Transactions, 1821, p. 209), conceived it necessary to pass the tar vapours through a red-hot tube. Indeed, ten years after its discovery, it was still a matter of speculation whether naphthaline existed in coal tar, or was a product of its decomposition, till Laurent (Annalen der Pharmacie, Bd. 3, p. 9, 1832) decided the question. But even then it was considered necessary to expose the tar to freezing mixtures, or to the action of chlorine gas, in order to make it yield up its naphthaline. It is probable that the tar of the London gas-works at present contains more naphthaline than that of former days. It may be useful to state that this interesting substance may be procured in enormous quantities at many of the tar-works, where it is deposited, mixed with paranaphthaline, by the oils distilled from the tar, in granular crystalline masses, called "salts," by the workmen. It is there thrown away as useless, or, at best, burned for lamp-black; and yet it is honoured in our chemical catalogues with a price of four or five shillings per ounce. In the tar of Scotland and the north of England, where cannel coal is much used, naphthaline is still a scarce article.

been discovered by Dumas,* and subsequently treated of by Laurent† under the name of anthracène. This substance is, perhaps, identical with the metanaphthaline which Pelletier and Walter‡ obtained from resin tar, and which it resembles in composition, as well as in many of its properties, though the latter authors were inclined to believe them different. Chrysène ($C_{12}$ $H_4$ ?) and pyrène ($C_{15}$ $H_6$ ?) are other solid hydrocarbons referred by Laurent§ to coal tar, but of whose exact character some doubt is still entertained.‖ The three last are among the least volatile part of the tar, and are probably the chief constituents of coal pitch, occupying the position which paraffine partly fills in wood pitch; they can be distilled only at temperatures above 300° C. (572° F.)

Of the liquid neutral oils of coal tar, which generally constitute about half the bulk of the tar, we have no precise information; and the present paper is intended as a contribution towards the filling of this hiatus.

The terms coal-naphtha,¶ and oil of tar, have generally been used

* Ann. de Chim., t. L, p. 182.

† Ibid. t. LX, p. 220; t. LXVI, p. 149; and t. LXXII, p. 415.

‡ Ibid. t. LXVII, p. 269.

§ Ibid. f. LXVI, pp. 136, 146.

‖ Laurent omitted to prove the existence of chrysène and pyrène in coal tar. He has described and analysed two substances, which he separated from the orange-coloured matter appearing among the last products, volatilized at a high temperature, from a sample of oil tar (Ann. de Chim., t. 66, p. 136). He assumed the identity of this product with the similar substance obtained from coal tar in the last period of distillation. This "yellow farina," as it is called by Kidd, appears to have been first noticed by that chemist, in his experiments on coal tar, which are recorded in his paper on naphthaline (Phil. Trans., 1821, pp. 212, 219). The last volatile products of the destructive distillation of a variety of organic matters present the same appearance, (see Bussy and Lecanu, on the "Distillation of Fixed Oils," Ann. de Chim., t. 30, p. 1, and other authors referred to by Laurent in the paper above cited), which has been aptly compared to that of realgar; but the identity of all these matters, though probable, requires demonstration. This substance has now been obtained in large quantities in a process of distillation of coal pitch, recently introduced by Mr. John Bethell, who has kindly supplied some of it, as well as of the other products of the tar, for an examination to which it is intended to submit this series of empyreumata, and which will form a subject for a future communication.

¶ The very loose application of the name "naphtha," which originally belonged to volatile hydrocarbonaceous liquids found at certain places in the earth, and which has since been adopted for the somewhat similar substance distilled from coal tar, as well as for the very different pyroxylic spirit, is productive of frequent inconvenience. A greater precision in our common nomenclature is highly desirable. It would be an improvement, perhaps, if the word "naphtha" were accepted as a generic term for liquid hydrocarbons of ascertained or probable pyrogenous origin, (or even without this restriction), and if a special prefix were always used to indicate the nature of every particular instance. Thus earth or native naphtha, schist naphtha, animal naphtha, &c., would be at once intelligible. Wood naphtha would designate the interesting hydro-

by chemical authors in a very indefinite manner, apparently from the want of precise notions of the nature of, and mode of procuring, these fluids. A short account, therefore, of the usual mode of treating the tar, and of the general nature of the products, may render more perspicuous the subsequent details.

*Of the products usually obtained from coal tar.*—Coal tar* is a black, thick, oily substance, insoluble in, and heavier than water, a considerable quantity of which, however, the tar usually retains in admixture. The distillation of coal tar is a regular branch of trade, and the operation is usually conducted in large iron retorts capable of holding many hundred gallons. The first products that come over are ammonia, and probably other permanent gases;‡ as the temperature rises, water charged with various ammoniacal compounds passes over, accompanied by a fetid yellow or brown oil, which floats on the water in the receiver. This oily matter gradually increases in quantity and density, and the water appears in smaller proportion; after some time, the oil distils over of such density, that it sinks in water; the receiver is now usually changed, and the

carbonaceous fluids of wood tar, and would leave the term "wood spirit" to the compound to which it is already appropriated, and which has already as many synonyms as can reasonably be required. Additional epithets would mark the distinct substances obtained from any one source: thus, in the case of coal tar, which yields two sorts of oil having the well-marked difference of being, one lighter, the other heavier than water, there would be light coal naphtha, and heavy coal naphtha, which terms will be adopted in this paper.

* The specific gravity of coal tar varies from about 1·120 to 1·150; the lightest samples containing the largest proportion of fluid oils. It exceeds most other tarry matters in density. The tar obtained in the distillation of beech, or oak wood, has a sp. gr. about 1·110. The tar from resinous trees is usually still lighter, Stockholm tar standing at about 1·040. A species of native tar, or petroleum, recently described by Dr. Ure (Pharmaceutical Journal, vol. 7, p. 485) as issuing from the earth in Derbyshire, is remarkably lighter than any of these, being of no greater sp. gr. than 0·900. Since the production of tar naphtha from coal by distillation, it has been a frequent and natural inference, that some of the many instances, in which petroleum and earth naphtha occur, were the results of destructive distillation going on in coal strata subjected to volcanic heat; and some authors have ventured to assert the identity of the artificial with the native product. The appearance in a coal mine (near Alfreton) of the substance just mentioned, rendered the question of its similarity to coal tar extremely interesting. The kindness of Dr. Ure, in offering a sample for examination, gave the opportunity of comparison. This specimen of the native tar was found to consist chiefly of fluid oils, boiling at temperatures above 300° C. (572° F.), containing scarcely any solid matter, and a very small quantity of oil boiling below 200° C. (392° F.) The physical characters exhibted by a cursory examination were thus quite sufficient to mark the substance as in every way distinct from ordinary coal tar. Its odour is entirely different from that of coal tar, or of any of its constituents, bearing, however, some resemblance to that of the oil distilled from bituminous schist.

‡ Vide not., p. 239.

previous oily distillate set aside as "light oil," or "crude naphtha." The tar generally yields from 5 to 10 per cent. of the "light oil," which will here be termed "light coal naphtha," or, for brevity, "light naphtha," when "coal" will be understood to be implied. As distillation proceeds, heavy oil continues to run, free from water, very fetid, and of a yellow colour. If much naphthaline is present in the tar, a large proportion of the earlier part of the heavy oil solidifies on cooling; frequently, however, the distillate shews no signs of solidification till a quantity of heavy oil, equal to about 30 per cent. of the tar, has come over; distillation always begins to flag at this stage, and the operation is usually stopped. The black residue which remains in the retort, and which solidifies into a hard vitreous mass on cooling, is "pitch," and is applied to the purposes of making asphalte, &c., or, when dissolved in a part of the distilled fluid, to the production of a black varnish much used for iron-work. The heavy oil, whose extraction forms the second period of the process, is technically called "dead oil," and will be referred to below as "heavy coal naphtha," or "heavy naphtha."

If the distillation is to be carried farther, a much higher temperature is required, and it is necessary to run off the pitch into smaller retorts. The product next obtained is, when cool, a greasy substance, of the consistence of butter, which is chiefly paranaphthaline; as the operation proceeds, the texture of the distillate becomes more resinous, and its colour yellowish. Finally, when the heat of the retort approaches redness, the vapours which escape from it condense in the form of a bright, orange-coloured powder, which is free from odour, and which, when pressed between the fingers, agglutinates into a viscous mass.* The residue now left in the retort is a beautiful coke, of a more or less porous structure, of extreme hardness, and difficult of combustion.

The heavy coal naphtha is seldom rectified; it is used chiefly for burning into lampblack, for coarse lamps or torches, and for the preservation of timber by impregnating it with the oil. Its antiseptic properties are remarkable, and may be owing partly to the hydrocarbons of which it chiefly consists, and partly to the carbolic acid, or to the creosote which it contains—(this, however, is not stated as affording any explanation of the fact). It contains aniline and leukoline, and probably other basic subtances less volatile than these, which are yet to be discovered.

The crude light coal naphtha is rectified, either by distilling it

* Vide not., p. 231.

from retorts, heated in the usual manner, or by driving steam through it; in either case, a further portion of heavy naphtha is separated from it as residue. The light naphtha thus rectified, has still a disagreeable smell, and, though colourless at first, gradually acquires a brown colour when kept, by the conversion of one or more of its components into non-volatile resinous matter. The coloration is usually, and with correctness, probably, assumed to be a result of oxidation. The light naphtha is further purified for commerce by treatment with some substance which removes the bad odour, to a greater or less extent, and completes at once the conversion of the colouring matter. The agent usually applied is oil of vitriol, which, on agitation with the distillate, acquires a deep red colour, with which it leaves the supernatant fluid more or less tinged. After another distillation, the oil should now be permanently colourless, free from naphthaline, and without offensive odour. It is evident, however, that by such treatment, some neutral substances, besides naphthaline, which, like that body, may have an attachment to sulphuric acid, may be removed, and would, therefore, be missed in an examination of the purified material of commerce.

*Of the product first examined.*—The subject of the first part of the present investigation was the crude light coal naphtha, as obtained from the tar distiller. Many samples of this product, from works in various parts of England, have been examined; and it is remarkable that the general constitution of all has been found to be the same;* the only manifest difference being in the quantity of naphthaline present, which, as before stated, varies greatly in different samples. This crude naphtha is a yellow or brown mobile fluid, of sp. gr. about 0·900 or 0·950,† rather redolent of ammonia, of picoline, and of other unpleasant bodies.

* There is much greater difference in the qualities of the "rectified naphtha," this depends upon the stage of the rectification at which the receiver was removed, and on the consequent exclusion or admission of the less volatile of the fluids, which will be described below: the quantity of sulphuric acid, or other decomposing agents, which have been used in the deodorizing process, of course also materially affects the character of the produce.

† The specific gravity of the product sold as "highly rectified," varies from about 0·860 to 0·900. The indications of the hydrometer are, to a certain extent, indicative of its purity, but they are very vainly, as well as universally, imagined by the distillers of coal naphtha to be as truly a criterion of the "*strength*" of their samples, as it is of the quantity of alcohol in spirit. What notion they attach to "strength," as regards a fluid not capable of dilution with water, is not very apparent. If they mean volatility, their test is erroneous, for all the hydrocarbons, except naphthaline, which the pure "light oil" ever contains, are nearly of the same specific gravity, the most volatile of all, however, being the heaviest, *i. e.* about sp. gr. 0·870; so long as the density of the

If distilled, it begins to boil generally about 100° C. (212° F.); and, as this continues, the temperature rises steadily up to about 200° or 220° (392°, 428° F.). The last portions of the distillate solidify on cooling, if much naphthaline be present (as is generally the case in naphtha made from London tar); and the residue in the retort is a dark brown resinous substance, resembling pitch. This, however, is not the same substance as the pitch residue of the tar above mentioned, but consists chiefly of the matter formed by the oxidation of some of the volatile fluids in the naphtha; so that, if the heat be urged farther, decomposition takes place, a red oil distils over, having a smell entirely different from that of any of the tar oils, accompanied by a small quantity of water, which is formed in the retort, but little or no paranaphthaline appears.

*Of the examination of the light coal naphtha.*—The method which was actually adopted in the laboratory for the separation of the substances in the *coal*-oil will be first described, as it is perhaps the only method which promises much security for the detection of all the fluids present in such mixtures. It is in principle the same as that which Faraday applied to the dissection of the *oil*-oil. The details here given will render unnecessary many repetitions, which would otherwise be requisite in future communications, in which it is intended to relate the results of an investigation of the other tar products. Subsequently, more compendious methods will be pointed out, by which some of the bodies, once detected, may afterwards be practically prepared for experiment. The object of this investigation being the neutral oils, the first step was to obtain them free from basic and acid substances. For this purpose, two gallons of the crude light coal naphtha were agitated frequently with a gallon of a cold mixture, of about nine parts of water, with one of sulphuric acid, which was so far diluted to destroy any tendency it might possess to decompose, or to form compounds with, the hydrocarbons. After the separation of the fluids, the oil was drawn off from the acid, and washed with water. It was then similarly treated with a dilute solution of potash, and again washed. This treatment with acid and alkali having been repeated, the oil had now lost much of its bad smell; an improvement in this respect having followed the application of each of these agents.*

liquid is greater than this, its sp. gr. will be an index of *purity*, (*i. e.* of its freedom from naphthaline, and from hydrocarbons having higher boiling points than that body, and from acid and basic oils, all of which increase its specific gravity, and, for the most part, diminish its volatility) but beyond this, the comparison is fallacious.

* Before treatment with acid, the light oil would tinge a piece of white deal yellow

The light naphtha thus purified, was distilled in convenient quantities of about a quart at a time in glass retorts, a thermometer being kept immersed in the fluid, and regular ebullition being constantly maintained. The boiling commenced at about 100° (212° F.) The thermometer continuing to rise constantly as the distillation proceeded; when the temperature had reached 150° (302° F.), about two-thirds of the contents of the retorts had distilled over, the greater portion of the remainder coming over below 200° (392° F.) When the mercury stood at a little above 200° (392° F.), the distillate began to solidify on cooling, and was now heavier than water. Attention is for the present restricted to the fluids received previously to the appearance of solid matter in the condenser. From similar results obtained from other samples, it was evident that, what is usually called, "coal naphtha" consists chiefly of a mixture of oils having boiling points below 200° (392° F.)*, (and, consequently, more volatile than naphthaline, which boils at 212°) (414° F.); so that the subject of present inquiry is conveniently defined. The distillates were mostly colourless, or nearly so, a pale yellow appearing in the latter portions, the brown colouring matter remaining concentrated in the residue. During the distillation, the receivers were changed at regular intervals of five degrees (9° F.) of increasing temperature.

A series of products were thus obtained, consisting of mixtures gradually decreasing in volatility. These were then submitted to a second distillation, in turn, commencing with the first received; the vessels were again changed at every 5th degree of heat (9° F.) in the retorts. A great depression was now observed in the point at which ebullition commenced in the case of each successive fraction, while, on the other hand, the thermometer index rose far higher than the superior limit of temperature, below which the same fluid was distilled in the previous treatment: for instance, the fraction which commenced from the boiling point 110° (230° F.) in the first order of operations, began to boil at about 90° (196° F.) in the second; while of the same portion, all of which was received below 115° (239° F.) in the first,

or, if the wood had been previously dipped in hydrochloric acid, purplish red. The first of these reactions was probably due to some salts of aniline; the second, perhaps, to the substance indicated by Runge as pyrrol. It had also the power of destroying the texture of the human cuticle, which Reichenbach mentions as belonging to creosote (Annalen der Pharmacie, Bd. 4, s. 275), and which is possessed more strongly by the crude heavy coal naphtha; so that the skin of the hands, after being touched with it, becomes dry and scales off. These properties had disappeared from the purified oil, which had, however, but little diminished in bulk.

* The heavy coal naphtha consists chiefly of hydrocarbons, boiling between 200° and 300° (392° — 572° F.), with more or less of paranaphthaline in solution.

more than a quarter remained unvolatilized at 120° (248° F.) in the second ebullition.* So that each fraction of 5° (9° F.) was distributed over 30° or 40° (54° or 72° F.) of the scale in the second order of receivers, in which the fractions corresponding to the same temperature from each successive retort of the second series, were mixed together, and kept separate from the others.

Thus a second series of distillates is presented; for each 5° (9° F.) from 90° to 200° (196° to 392° F.) In the same manner this series is again dispersed over the range of boiling heats, by a third succession of distillations, and again collected in a separate set of receivers. The depression of the first boiling point is now lessened, and the extent of scale traversed by the thermometer is more contracted in each separate retort, than in the preceding series. An approach towards purity, or, at least, towards an inferior degree of complexity is thus attained in each fraction. New series of distillations, conducted in the same manner, give successive advances in the desired direction.

Of the first order, all the fractions were almost exactly of the same bulk, especially between 100° and 170° (212° and 338° F.) In each later series, however, a greater quantity distilled over at certain temperatures than at others, so that the points of most copious produce converged towards certain centres of temperature, indicating clearly that, in the naphtha, the quantity of fluids, having boiling points near such temperatures, was much greater than that of fluids having intermediate stations.

*Of the results of the examination.*—Thus, after ten distillations of the whole quantity, a series of fluids were obtained, having boiling temperatures between 60° and 190° (140° and 376° F.); and of these, the *maxima* were between 60° and 70° (140° and 158° F.), between 80° and 85° (176° and 185° F.), between 110° and 115° (230° and 239° F.), between 140° and 145° (284° and 293° F.), and between 170° and 175° (338° and 347° F.) So that the fractions corresponding to some of these temperatures, were about three times as great as some of the others. The boiling *spaces*, within which any

* This inevitable result of the distillation of a medley of fluids in solution in each other, has, in some cases in which it has been observed, given rise to the notion, that, on each ebullition, a fluid, which has been assumed to be a definite compound, has been decomposed into other products, some more, some less volatile than the original substance. (Vide Pelletier and Walter, Ann. de Chim., t. 67, p. 269, on Retinole, where it will be seen that their observations on this subject throw doubt on their analysis of their supposed pure hydrocarbon.) During all the distillations to which the coal-oils have been submitted in the present treatment, nothing has appeared that could cause the slightest suspicion, that they, at their boiling temperature, under ordinary pressures, have ever the faculty, like amputated earthworms, of growing into separate bodies, or, like star-fish vexed, of casting off their unoffending members in spasmodic suicide.

one of these would now distil, were very much contracted, but not yet reduced to *points;* more than half of each quantity coming over within the limits of its previous ebullition,—thus, of 15 ozs. received from the ninth series of retorts between 110° and 115° (230° and 239° F.), nearly 8 ozs. distilled between the same limits on the tenth rectification, ebullition commencing at 106° (223° F.), and not ½ oz. remaining in the retort at 120° (248° F.) The operation was always stopped when the distillate, from the less volatile oils, began to solidify in the condenser, so that, from the last fractions of each series, a quantity of naphthaline, less on each successive rectification, was eliminated, till it finally disappeared from all the fluids obtained at temperatures below 190° (376° F.).

In the earlier distillations the retort-contents acquired, as ebullition continued, a pale brown colour, especially in the fractions between 130° and 160° (266° and 320° F.), and the colouring matter remained in the retorts as residue. The more volatile liquids left no residue in the later distillations. All the products were colourless; but those, even of the tenth order, that came over about 140° (284° F.), after being kept some time in glass bottles, became slightly coloured, and deposited a brown film on the glass, though the others remained clear as water. The specific gravities of all the fluids were nearly the same, when the less volatile were quite free from napththaline; all having a sp. gr. between 0·86 and 0·88. The most volatile of all having, however, the greatest density. Those which are marked by preponderance in quantity over the others have peculiar odours, by which they may be at once distinguished from each other by a person accustomed to them, though, to an indifferent observer, they all smell alike—of "naphtha." These odours merge gradually into each other in the intermediate fractions; those of the more volatile oils are the most powerful, and of an ethereal character; those less easily vapourised being rather aromatic. The most volatile of all the products differs, however, remarkably in this respect from the rest. The maxima about 70° and 170° (158° and 376° F.), were not nearly so great as those about 85°, 115°, and 140° (185°, 239°, and 284° F.); that belonging to 170° (376° F.) being deficient, because the greater part of the oil which it represents remains mixed with the heavy naphtha, by which it is kept back on the distillation of the tar.

There is no doubt, then, that at least five distinct fluids enter into the constitution of the light coal naphtha; and it is possible that others will yet have to be added to the list. Each of these substances demands separate consideration.

*Of the oil boiling about* 60°-70° (140°-158° F.)—This liquid is characterized by a peculiar alliaceous odour, somewhat resembling that of bisulphide of carbon, entirely different from that of all the other substances in the naphtha. It is so extremely volatile, that it is probable that on each distillation a portion of it escaped condensation; this, indeed, appeared to be the case.* So small a quantity of it exists in the naptha, that not more than an ounce was obtained from the two gallons of the crude material used in the investigation. Its examination is, therefore, deferred for the present, till a sufficient quantity has been prepared by the treatment of a large supply of the most volatile part of the crude distillate from the tar. It is by no means certain that it consists of only a single very volatile fluid, mixed with a certain quantity of the oil received at about 80°-85° (176°-185° F.) It may be mentioned, however, that the greater part of it forms a compound with oil of vitriol, from which water precipitates a solid substance, having an aromatic odour.

Attention was accordingly turned to the most volatile product that appeared in quantity sufficiently large to encourage examination.

*Of the oil boiling about* 80°-85° (176°-185° F.)—The comparatively slow rise of the temperature, in the retorts, between 80° and 90° (176° and 194° F.), even in the fourth series of distillations, indicated that the fluids received between those limits was of far simpler constitution than at first, and that a considerable quantity of some

* It has been remarked above, that coal tar probably contains permanent gases (besides ammonia) in solution. It seems not unlikely that the same is true of the more volatile hydrocarbonaceous liquids distilled from it, even after several rectifications; for the fluid in condensing would, of necessity, carry down with it a certain quantity of such gases as were mixed with its vapour, and are copiously soluble in the fluid, while, at the same time, a certain quantity of the vapour of the liquid would escape in solution in the liberated gas. This reflection, supported by Faraday's experiments on the fluids compressed from oil gas (Philosophical Transactions, 1825), and by those of Couerbe on the similar products obtained from resin gas, (Comptes Rendus, v. 7, p. 497), provokes the conjecture that an investigation undertaken with coal gas, by submitting it to powerful condensation, (especially when taken fresh from the hydraulic mains or from the cooling apparatus, and before it has undergone any purifying process), would be rewarded by the detection of some hydrocarbons not hitherto observed:—bodies whose physical state at ordinary temperatures may lie on the verge between the liquid and the gaseous, and whose chemical nature may fill the gap between the simple constitution of marsh gas, or olefiant gas, and the far more complex arrangement of the simplest known hydrocarbon of the tar liquids, the density of whose vapour is to that of olefiant gas as 2·78 to 1, and to that of marsh gas as 4·87 to 1, while its boiling point lies perhaps 200° (392° F.) above that at which either of these latter liquefies. (Sp. gr. of benzole vapour, 2·770; of olefiant gas, 0·985; of marsh gas, 0·559.)

compound was present, whose boiling point was in this immediate neighbourhood.

Mr. Faraday long ago suspected the presence in coal tar of the "bicarburetted hydrogen," which he discovered in the oil gas liquor; he mentions, however,* that his search for that substance in coal tar was unsuccessful. Some samples of coal tar contain a very much smaller proportion of the more volatile liquids than others; so that the unfortunate escape of this substance, from the acumen which then threatened its detection, was probably owing to the inquiry having fallen upon unfavourable specimens. However, the subsequent production of the same oil, by Mitscherlich,† from benzoic acid, from which it has derived its present patronymic (benzole), having exhibited the true nature of its constitution ($C_{12}$ $H_6$), and the development of organic chemistry having farther revealed its properties, after twenty years another scrutiny was not to be evaded. Thus Dr. A. W. Hofmann‡ was enabled to shew the existence of benzole in coal naphtha, by means of the test for its presence, which he deduced from its convertibility into aniline. He did not, however, at that time attempt to separate this hydrocarbon from its associate tar-oils.

The observations of Faraday and of Mitscherlich had informed us that this compound boiled at 85°·5, or 86° (186° or 187° F.), and that, like water, it solidified at 0° (32° F.) From these facts, and from the habitudes of the light coal naphtha above described, it was clear that the benzole was to be looked for among the more volatile of the fractions obtained.

*Of the preparation of benzole from coal naphtha.*—The fifth series of the distillations, just spoken of, yielded about a pint of fluid, which had boiled between 80° and 90° (176°-194° F.) It was clear and colourless, of a powerful spirituous odour, in which a refined sense would recognise the fragrance of benzole, though a vulgar organ might be reminded of coal gas.

A small quantity of the fluid received on the fifth distillation between 85° and 90° (185° and 194° F.), being exposed to cold, at about five degrees below 0° (32° F.), in a test-tube, soon became in part solid and crystalline. The fraction received between 80° and 85° (176° and 185° F.) behaved similarly, while specimens corresponding to temperatures below 80° (176° F.) and above 90° (194° F.), shewed

* Philosophical Transactions, 1825, vol. 115, p. 465.
† Annalen der Pharmacie, 1834, Bd. 9, s. 43.
‡ Ibid. 1844-5, Bd. 55, s. 43.

no signs of solidification, except such of the least volatile as contained naphthaline, which they partially deposited. On being submitted, in a freezing mixture, to a temperature of—20° (4° F.), the sample representing the boiling *line* 75°-80° (167°-176° F.) yielded a portion of crystalline matter, and those from 80°-90° (176°-194° F.) became almost entirely solid, while those from 90°-95° (194°-203° F.), and upwards, still suffered not the slightest change of state.

It was now almost certain that benzole was secured, and that the solidification was due to that substance. It was evident, however, that the crystalline product thus obtained would be a mixture of the desired matter with substances having boiling points more or less near to that of the hydrocarbon, in which they were present as impurities; and, that, unless these fluids had the same freezing point as benzole, or would form compounds with it which are solid at the same temperature, they might be separated from it by pressure and filtration. The whole of those fractions of the fifth order of distillates, which had been received between 80° and 90° (176°-184° F.), were treated accordingly.

A very simple apparatus—one of Beart's coffee-pots—effected the purpose. This machine consists of a hollow cylindrical vessel, into which a perforated piston fits tightly, supporting a piece of strong cloth, so as to form an apparatus, in which rapid filtration is effected by the atmospheric pressure, when the piston is forcibly raised through the fluid. The application is obvious. The filter-piston is placed at the bottom of the vessel, which is immersed in a mixture of snow and salt. The fluid to be purified is now poured into the pot, or, better still, is first exposed, in large test-tubes, to the freezing mixture, and from them, when solidified, is transferred to the filter. The crystalline mass may be expelled from the tubes very readily, by holding their mouths downwards, and slightly warming their sides and closed ends with the hand, when a minute quantity, becoming vapourized, will expand, and will force out the solid in the form of mould candles of benzole. The temperature is kept at about 10° or 12° below 0° (14°-11° F.) in the filtering vessel, while its contents are stirred and broken down, to prevent passages being left for the air through the mass when the piston is raised, it being essential that the pressure of the substance against the filter should be as great as can be ensured.

When the piston is drawn up, a crystalline mass, like snow in whiteness and texture, is separated from the fluid oil which has passed through the filter. This product is placed in a funnel, the bulb of a thermometer being buried in it, and the temperature is

allowed to rise slowly while the thawing fluid is received below. The melting proceeds rapidly at first; more slowly as the temperature approaches $0^0$ ($32^0$ F.), which point it will pass before the whole has fused. The receivers are changed at intervals of increasing temperature, and their contents, being separately subjected to another refrigeration, and again liquefied in like manner, yield further portions which remain solid above $0^0$ ($32^0$ F.). These last, together with that which in the first instance was still congealed at $0^0$ ($32^0$ F.), prove to be nearly pure benzole. It is usually found that the thermometer indicates $4^0$ or $5^0$ above $0^0$ ($39^0$-$41^0$ F.) before all the substance in contact with its bulb is fused. The portion that quits the solid state last, is found to be a fluid which crystallizes now at a temperature a little above $0^0$ ($32^0$ F.), and boils *constantly* at $80^0$ ($175^0$ F.) in glass vessels with pieces of platinum wire at the bottom, distilling over without leaving a trace of residue in the retort. It is, therefore, a pure substance.

It remains to confirm the identity of this substance with benzole, which its properties so strongly indicate.

This fact is supplied by an analysis, which was made by Mr. E. C. Nicholson, of the fluid thus prepared, the results of which were:

When burned with protoxide of copper,

0·2028 grm. of substance gave
0·6840 „ „ carbonic acid, and
0·1405 „ „ water.

Percentage of components,

| | |
|---|---|
| Carbon . . . . . | 91·98 |
| Hydrogen . . . . . | 7·69 |

The constitution of benzole, as calculated from its admitted formula,

$$C_{12}\,H_6,$$

being

| | | |
|---|---|---|
| 12 equiv. of Carbon . . . . | 72 | 92·3 |
| 6 „ „ Hydrogen . . . . | 6 | 7·7 |
| 1 equiv. of Benzole. . . . . | 78 | 100·0. |

By subsequent rectifications of the naphthas, whose boiling *lines* in the fifth series of distillations had extended some distance above $90^0$ ($194^0$ F.), a further produce of fluid, crystallizable by the above process, was obtained, so that the two gallons of light coal naphtha yielded about a pint of nearly pure benzole.

*Of some of the physical characters of benzole.*—The fluid thus isolated, though readily crystallizable at 0° (32° F.), may be cooled to a temperature considerably lower, in a smooth glass vessel, kept still, without change of state; but if, when in this condition, it is agitated, especially if poured into another vessel, it will instantly congeal. When rapidly solidified, it presents the appearance of a crystalline white wax, or of camphor, like which substance it will take fire at a flame, and will burn without immediately fusing. When cooled very slowly, it crystallizes in beautiful cruciform leaflets, of perfect transparency, which aggregate into forms resembling fern-fronds, with numerous pinnæ at right angles to a principal axis.

Repeated experiments have shown that it boils, at ordinary pressures, at a temperature a little above 80° (176° F.), but not higher than 81° (178° F.)*; and it is worthy of remark, that a sample of benzole, prepared from benzoic acid by Dr. Hofmann, observed by the same thermometers, in glass vessels containing metallic fragments, boils at the same point. The observation of Mitscherlich† had placed the boiling point of benzole at 85°·5 (186° F.), and Faraday† found that his "bicarburet of hydrogen" boiled at 186° F. (85°·5 C.) "in contact with glass." It is difficult to account for these discrepancies, unless the explanation suggested by the clause just quoted from Faraday's account is sufficient.

An experiment made to ascertain the specific gravity of its vapour gave the number 2·823, for which Mitscherlich's probably more correct determination gives 2·770, and calculation 2·737.

Its odour is identical with that of the hydrocarbon yielded by benzoic acid when distilled with an excess of lime. It is extremely inflammable, the vapour arising from it readily taking fire on the approach of a flame near to the surface of the fluid; an enormous quantity of carbon being evolved in the combustion. A current of hydrogen passed through the fluid will burn with an intensely white flame; oxygen, similarly treated at the ordinary temperature of the air, forms, with the vapour which it takes up, a mixture of tremendous explosive power. Atmospheric air, charged with the vapour,

* Since these observations were made, by which the boiling point of benzole was thus placed at 80° (176° F.), Kopp has published some elaborate researches on certain properties of some fluids (Pogg. Annal. Bd. 72, s. 1 und 223). One of the express purposes of his experiments being the exact determination of boiling points, the greatest confidence is claimed by his results. His statement is, therefore, valuable in confirmation of the fact here noticed. The conclusion which Kopp draws from his observations, which he details at length (op. cit. s. 240), is that the boiling point of benzole is 80°·4 (177° F.), at 760 mm. bar.

† Locis sup. cit.

will burn with a smoky flame, with a pure white light, or with a beautiful violet-blue flame, according to the size of the jet from which it issues, and the velocity with which the stream enters the surrounding air: a given quantity of air taking up more of the vapour than it can itself consume.*

The specific gravity of the fluid is 0·85. It is extremely mobile, the bubbles, formed upon a surface of it when shaken, breaking instantly before the fluid becomes tranquil: in this respect it differs remarkably from the cognate hydrocarbons having higher boiling points, which retain their bubbles longer, according to their weaker volatility, those highest in the scale reflecting most gorgeous iridescent colours from the films of liquid. These latter also exceed benzole in the power of refracting light, though that fluid has this character strongly marked.

*Of some useful properties of benzole.*—Benzole dissolves many substances with extreme readiness, and in large quantities, such as many resins, mastic, camphor, wax, fatty and essential oils, caoutchouc and gutta percha. Its strong volatility gives to its solution of either of the two latter substances, the useful property of drying rapidly and perfectly, so that, when spread on glass or any polished surface, a film of the gum is deposited, which may readily be peeled off in the form of a tough membrane of any required degree of tenuity, and possessing all the properties of the original material. The same solutions varnished on the skin, form admirable artificial cuticles, which have been found useful in cases of wounds and burns, and might probably be very beneficial in some skin diseases.

It dissolves gamboge in smaller quantity, and shell-lac even more sparingly: but it will mix in equal bulks with a saturated solution of lac in wood spirit or alcohol; this property may be valuable to varnish makers.

Copal and animè yield but slightly to the solvent power of this fluid; but its vapour, in the act of condensation, rapidly dissolves these resins;† so that, if fragments of them be suspended in the head

* The different volatility of the other coal naphthas which will be here described, (as well as of liquid hydrocarbons generally), is well illustrated by their relative inflammability. Their habitudes, in this respect, are strikingly different from that of benzole. The fluid boiling about 110° (230° F.) will take fire on its surface, at ordinary temperatures, from a flame, but yields so little vapour to a current of common cool air, that this will burn only with a blue flame. The oils boiling at 145° and 170° (293°—338° F.), afford so little combustible matter to an air stream, as to show no flame at all at the jet, nor will the surface of a stratum of either of them in an open vessel kindle at a match, but will extinguish a burning body plunged into the liquid; in this behaviour they resemble oil of turpentine which boils at 155° (311° F.).

† The interesting physical fact, of this property of certain vapours, was pointed out to

of a vessel, in which the hydrocarbon is boiling, the vapour, as it condenses on their surfaces, softens and dissolves them, and trickles back into the vessel below, in which a colourless varnish will result, more or less concentrated according to the duration of the process.

Benzole dissolves quinine, depositing it on evaporation in a crystalline form; the condensing vapour dissolves the alkaloid, especially if not recently precipitated, more readily than the boiling liquid. Cinchonine it does not dissolve, but forms with it a bulky gelatinous mass. It dissolves strychnine and morphine, but sparingly.

It dissolves iodine, phosphorus, and sulphur; and, when boiling, takes up the latter in large quantity, of which, however, the greater part crystallizes out as the fluid cools.

It has been found extremely useful in the laboratory as a solvent, in researches in organic chemistry; where the high price, and almost too great volatility, of ether, render a substitute for that agent a frequent desideratum.

It has an interest, too, as offering a cheap and ready source of many of the organic compounds of the benzoic series. Several beautiful bodies, which, from the comparative costliness of the parent materials, had only been obtained previously in very small quantities, may now be prepared in large bulk; such as nitro-benzole, nitraniline, &c. Dr. Hofmann has recently used coal tar benzole, prepared by a method which will be described below, as a convenient source of aniline, of which base he has thus produced a large quantity for some researches in which he has been engaged.

The facility with which the vapour of benzole is taken up and retained by the air at its ordinary temperatures, has been mentioned above. This property has been made to do service, with great success, in an apparatus for illumination, in which a stream of air, having passed through a reservoir of the volatile hydrocarbon, is conducted through pipes to the burners, at which, being ignited like coal gas, it yields a light of extreme brilliancy and whiteness.

The property possessed by alcohol and pyroxylic spirit of burning with an almost lightless flame, so opposite to that of the highly carbonized benzole, renders it easy, by properly adjusting a mixture of the volatile oil with either of these spirits, to obtain a fluid which shall be readily vapourized, and shall yield a flame of any required degree of whiteness. Thus a mixture of one part, by measure, of

the writer, as belonging to oil of turpentine, by Mr. Robert Beavan. It seems worthy of more extended knowledge and inquiry. M. Daguerre, in some of his early photographic experiments, found that the vapour of petroleum dissolved certain resins more readily than the liquid.

benzole, and two parts of spirit of sp. gr. about 0·840, forms an excellent fuel for a portable gas-lamp, which supplies itself with vapour by the heat which it generates in combustion. Any excess of spirit diminishes the luminosity of the flame; while too much of the other causes a tendency to smoke. Similar mixtures may be made of benzole with acetone, or with other inflammable liquids poor in carbon. The other hydrocarbons of coal tar are more or less soluble in alcohol and wood spirit, but benzole appears to be more copiously miscible with spirits containing a given amount of water than most of the others; and it is far more so than oil of turpentine.* The oil requires, of course, a much larger quantity of acetone, than of the spirits† of the ethyle and methyle series, to effect the due reduction of the amount of carbon in the fluid; as will be evident by a comparison of their formulæ reduced to a common denominator for hydrogen.

| | |
|---|---|
| Acetone . . . . | $C_6 H_6 O_2$ |
| Alcohol . . . . | $C_4 H_6 O_2$ |
| Pyroxylic spirit . . | $C_3 H_6 O_3$ |

The inhalation of benzole vapours for the production of insensibility to pain is already on record as effectual. In the instances in which it has hitherto been administered, the material prepared from benzoic acid has been found to induce certain phenomena of irritation.‡ Dr. Snow, who has recently tried the effect of coal benzole on mice, has found that it "causes insensibility, but accompanied with convulsive tremors." It is possible, however, that this substance, either alone or mixed with the volatile fluids, may yet aspire to become, if not to receive, the "popularis aura."

* The fuel burned in the vapour-lamps of Lüdersdorff, which are in use in some parts of the Continent, consists of oil of turpentine dissolved in alcohol. It is necessary, however, to use very strong alcohol to retain this hydrocarbon in solution, or to distil the two fluids together with certain precautions; and the price of both of these ingredients (or of wood spirit sufficiently free from water to dissolve oil of turpentine) is too high in this country to permit this mixture to be consumed. This is not the case with the ingredients mentioned above. The volatility of benzole—so much more nearly similar to that of the spirits—renders it additionally superior to most other hydrocarbons for this purpose.

† It is remarkable that the power of spirits, as solvents for hydrocarbons, seems to bear some inverse relation to the amount of oxygen in the composition of the former, while the solubility of the spirits in water increases in the other direction. Thus oil of turpentine is dissolved by acetone far more readily than by alcohol; and benzole, which is insoluble in alcohol much diluted with water, will expel the water from acetone with which it may be mixed, and will take its place in solution. Again, if to such alcoholic or pyroxylic spirit as will dissolve benzole or some of the other coal naphthas, but refuses to take up oil of turpentine, a small quantity of benzole be added, the spirit will acquire the property of dissolving the oil of turpentine.

‡ Dr. Snow, in Lancet, 1848, February 12; and Professor Simson, in Pharmaceutical Journal, 1848, May.

The promises which benzole makes of utility, are sufficiently numerous to encourage a belief that it may form a special object of manufacture and of commerce. It may be procured to any extent from coal tar or from the light naphtha, in which it has hitherto been "wasting its sweetness on the desert air." If absolute purity be not required, it may be prepared, with very little expense and trouble, either in the laboratory, or, on the large scale, in vast quantities, and by a farther slight outlay of time, any required degree of purity may be ensured in the product. The description of a method which has been found to yield very satisfactory results may not be devoid of interest.

*Of a practical mode of preparing benzole.*—The boiling point of benzole is the same as that of alcohol of sp. gr. 0·825 (176°* F. = 80° C.); it is evident, therefore, that any of the summary processes of rectification which are practised by distillers in the manufacture of alcoholic spirits, are applicable to the separation of benzole from the less volatile fluids of the naphtha. The method now to be described is, one which extracts nearly the whole of this spirituous hydrocarbon, by a very slight expenditure of time.

The light coal naphtha (of which it is convenient to take a sample which came over at the commencement of the distillation of the tar, which contains the benzole less diluted with substances having higher boiling points) is placed in a metal retort, which is surmounted by an open vessel filled with water, and containing a worm or chamber, into which the vapour of the naphtha passes directly from the retort, and so arranged that the less volatile fluids, which will be condensed in it, will flow back into the retort, or into a separate receiver, while the fluids more volatile than water will pass on in vapour to another condenser, which is kept as cold as possible. The water surrounding the still head will gradually rise in temperature as the operation proceeds, and will at last boil; and when this takes place, (or if the heating of the water be checked at any period of the process, by addition of cold water,) distillation will cease, for no fluid remains in the retort whose vapour is not condensible at the temperature of the head, which can never rise above 100° (212° F.). The distillate being rectified a second time in such an apparatus, keeping now the temperature of the head at or a little below 80° (176° F.), and reserving the part which comes over before the temperature in the retort has passed 90° (194° F.), a large proportion of a very volatile oil will be obtained, which, when exposed

* Ure, Dictionary of Chemistry, ed. 1835, art. Alcohol, p. 131.

to a temperature of—20° (4° F.), will become solid to at least half its bulk. Of course, if the apparatus be double, the same result may be obtained by a single operation. A comparatively small quantity of a similar product may be obtained by receiving separately the first two or three gallons that run off from the common stills on the rectification of some hundred gallons of the light naphtha.

This produce should then be agitated with about a quarter of its bulk of oil of vitriol, or, better still, with about one-tenth of strong nitric acid, and then, after separation from this agent, with oil of vitriol, as above. It should then be separated from the acid and distilled (or it may be distilled from the sulphuric acid), reserving again the portion given off below 90° (194° F.). The distillate, being tested by agitation with oil of vitriol, should remain perfectly colourless, and the acid should not now acquire a darker colour than a pale straw-brown; if it acquires a deeper tint, the process should be repeated. When this result is obtained, the oil should be well washed with water, and, finally, with an alkaline solution.

Its farther purification may now be entrusted to its congealing property. It should be exposed to a temperature of about—20° (4° F.), (which may be conveniently attained by a mixture of ice and salt); the solid portion being then pressed and filtered, the result, after treatment with chloride of calcium, is fit for use.

The use of sulphuric acid in this process is to remove all the basic substances present, to oxidize the brown colouring matter (of which, however, but a small quantity accompanies the most volatile part of the light coal naphtha), and to remove such of the neutral oils as form compounds with oil of vitriol.* Among these latter, the alliaceous oil, which has been before mentioned, more volatile than benzole, is withdrawn, while the latter entirely resists the action of this acid, even on being boiled with it. The nitric acid assists in the removal of the oxidable substances, and by forming a small quantity of fragrant nitro-benzole (which is left behind as residue on the distillation of the fluid), improves the odour of the product.

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It has been stated above, that from the light coal naphtha other oils have been obtained in considerable quantity, boiling about certain special temperatures. These have not yet been subjected to the careful

* The compounds formed with sulphuric acid by some of the oils in the coal naphtha, promise subjects for future examination; some of them are certainly coupled acids, probably analogous to hypo-sulpho-naphthalic acid, as has been before observed by Blanchet and Sell, (Annalen der Pharmacie, Bd. 6, s. 312).

examination which they demand, which, however, it is intended to pursue. Three of these, however, are so decidedly marked as distinct, that they may be mentioned in anticipation of future details.

*Of the oil boiling about* 110°-115° (230°-239° F.)—At a very early stage of the rectifications, which have been described in a former section of this paper, an excess of distillate was observed to affect this part of the scale, and the few following degrees. In the later series the point of convergence appeared to lie about 113° (235°·5 F.): a very large fraction has been obtained corresponding to this temperature. This oil has not yet been isolated in a state of absolute purity, so as to claim an analysis: indeed, it has not yet been made the subject of special attention. The basic substance, however, which is obtained from it, by the action of reducing agents on its nitro-compound, proves to consist almost entirely of well crystallized toluidine; so as to leave no doubt that toluole ($C_{14}$ $H_8$) is one of the chief constituents of the light coal naphtha. Dr. Hofmann has used some of the oil, separated from the naphtha by distillation, at the temperature here indicated, as a source of toluidine, for some experiments in which that substance was requisite. The boiling point of benzoène (toluole), which Deville obtained by distilling the resinous part of tolu balsam, was fixed by him at 108° (227° F.)* Mr. Noad found the toluole which he prepared from toluidic acid to boil between 109° and 110° (228°-230° F.)†

*Of the oil boiling about* 140°-145° (284°-293° F.)—The maximum of distillate, which is most decided in the higher part of the series, is received between 142° and 145° (288°-293° F.) This oil presents all the characters of cumole ($C_{18}$ $H_{12}$). The boiling point of the hydrocarbon, obtained by distilling cuminic acid with an excess of caustic lime, was fixed at first by Gerhardt and Cahours at 144° (291° F.)‡ Mr. F. A. Abel has recently placed it at 148° (299° F.)§ Should the naphtha oil now spoken of prove to be the same substance, its production in large quantity may aid the determination of the question.‖

* Annales de Chimie; sér. 3, t. III, p. 169.

† Philosophical Magazine, vol. XXXII, p. 32.

‡ Annales de Chimie; sér. 3, t. I, p. 60.

§ Philosophical Magazine, vol. XXXII, p. 66.

‖ The existence of toluole and cumole in coal tar is interesting, as shewing the similarity between this substance and the resin tar, in which both of these fluids were detected by Pelletier and Walter, and described by them under the names of retin-naphtha, and retinnyle (Ann. de Chim. t. 67, p. 269). They also found much naphthaline, and described an oil boiling about 240° (230° F.), belonging to the resin tar. It is extremely likely that this last matter was a mixture of oils similar to a part of the neutral fluid of the heavy coal naphtha: and there is little doubt that their meta-naphthaline was an impure specimen of paranaphthaline. It has been remarked above, that these authors probably missed some of the hydrocarbons present in their material; so that it is probable that the points of contact between the two productions may be

*Of the oil boiling about* 170°-175° (338°-347° F.)—The next favourite point lies between 170° and 172° (338°-342°) F.); and the fluid, which distils over at this temperature, bears so strong a resemblance in odour and in other properties to cymole ($C_{20}$ $H_{14}$), the boiling point of which Mr. Noad observed to be at 171°·5 (341° F.),* as to induce the belief that this body is identical with the hydrocarbon existing in cumin oil. This oil, though by its nature (sp. gr. 0·857) referrible to the light naphtha, in which it is found, as above remarked, only in small proportion, is largely contained in the heavy coal naphtha, from which it is intended to prepare it, hereafter, for examination.

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If these latter hydrocarbons be correctly assigned to the places of toluole, cumole, and cymole, it will be an interesting fact, that coal tar contains, among its chief constituents, the only four members yet known of the series of hydrocarbons which are represented by the formula:

$$C_6 + n\,(C_2\,H_2),$$

in which $n$ represents successively the order of natural numbers, the lowest known term of which is that in which $n=3$,—(Benzole). It may seem, too, not improbable that the gap, which chemistry has not yet filled (where $n=5$), the boiling point of whose corresponding oil would probably lie between that of toluole and cumole, may yet find its occupant in the coal naphtha. It may be hoped, too, that this fruitful source of the compounds alluded to, may not long leave, *sub judice*, the theory of the successive increments of temperature, necessary for ebullition, which is due to each successive factor, of $C_2$ $H_2$, introduced into the composition of the fluids.

Nor is the remark unworthy of citation here, that a close relation seems to exist between three of the tar compounds—one from each of the three classes—thus,

| | | | | |
|---|---|---|---|---|
| Neutral, benzole | $C_{12}H_6$ | $=C_{12}H_5, H$ | hydride | of phenyle |
| Basic, aniline . . | $C_{12}H_7N$ | $=C_{12}H_5, NH_2$ | amide | |
| Acid, carbolic acid | $C_{12}H_6O_2$ | $=C_{12}H_5, O, HO$ | hydrated oxide | |

It may be useful to exhibit the constitution of coal tar in a tabular form, representing the boiling points of the various substances contained in it, which will indicate the part of the products in which any one of the substances is to be looked for when the distilling temperature is indicated by a thermometer.

more numerous, if indeed their neutral parts be not altogether identical. Benzole, however, did not appear among the resin oils, although it is by no means unlikely that this oily spirit, being present, slipped unnoticed through the hands of the observers.

* Philosophical Magazine, vol. xxxii, p. 18.

## SUBSTANCES CONTAINED IN COAL TAR.

| Centig. Therm. scale. | Neutral. | Basic. | Acid. | Tar Products. |
|---|---|---|---|---|
| 50 | ? Alliaceous oil | ? Pyrrol, ? | | Light-oil, or "Naphtha." |
| 70 | | | | |
| 80 | Benzole, $C_{12} H_6$ | | | |
| 100 | | | | |
| 111 | | Picoline, $C_{12} H_7 N$ | | |
| 113 ? | Toluole, $C_{14} H_8$ | | | |
| 148 ? | Cumole, $C_{18} H_{12}$ | | | |
| 171 | Cymole, ?, $C_{30} H_{14}$ | | | |
| 182 | | Aniline, $C_{12} H_7 N$ | | |
| 187 | | | Carbolic acid / Hydrate of phenyle $C_{12} H_5 O, HO$ | |
| 200 | | | | |
| 212 | Naphthaline, $C_{20} H_8$ | | | Heavy-oil, or "Dead-oil." |
| 220 | | | | |
| 239 | Various liquid Hydrocarbons | Leukoline $C_{18} H_9 N$ | | |
| 280 | | | | |
| 300 | | | | |
| ? | Paranaphthaline, $C_{30} H_{12}$ ? | | | Pitch. |
| ? | Pyrene ?, $C_{15} H_6$ ? | | | |
| ? | Chrysene ?, $C_{12} H_6$ ? | | | |

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